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FAKULTA CHEMICKÁ
ÚSTAV FYZIKÁLNÍ A SPOTŘEBNÍ CHEMIE

FACULTY OF CHEMISTRY
INSTITUTE OF PHYSICAL AND APPLIED CHEMISTRY

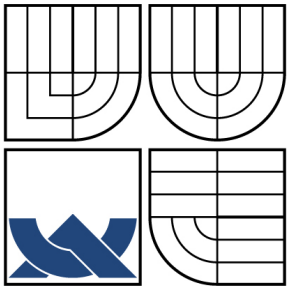
THE ANTIOXIDANT EFFECT OF HUMIC ACIDS

DIPLOMOVÁ PRÁCE
DIPLOMA THESIS

AUTOR PRÁCE
AUTHOR

BARBORA BAKAJOVÁ

BRNO 2008



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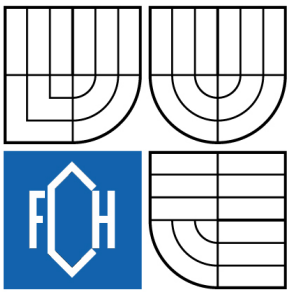

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DIPLOMA THESIS

AUTOR PRÁCE — BARBORA BAKAJOVÁ
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Barbora Bakajová	Ing. Jiří Kučerík, Ph.D.	
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Děkan fakulty

ABSTRACT

The main aim of the thesis was to study influence of humic acids and its salts on the thermo-oxidative stability and degradability of polyvinyl alcohol (PVA). For this purpose, thermogravimetry was employed. It has been demonstrated that small concentrations of humic acids caused an increase in stability of investigated PVA. In contrast, high concentrations showed only a slight stabilizing effect, in some cases the presence of humic acids lead even to the PVA destabilization. In the second part, the durability of polymer material was adjusted by the γ-irradiation pretreatment. Obtained results indicated that presence of ammonium and sodium salts of humic acids caused a significant stabilization of the polymer material in comparison with the pure PVA and showed the stabilizing effect even after a long term γ-irradiation exposition. The last task was to evaluate the ageing effect on the PVA/humic blends. It has been showed that no additional chemical reactions occurred in PVA/humic acids blends and thus the prepared material showed the constant physical properties during the several-months experiments.

ABSTRAKT

Hlavním cílem diplomové práce byla studie vlivu huminových kyselin a jejich solí na termooxidační stabilitu a degradabilitu polyvinylalkoholu (PVA). Pro tento účel byla využita metoda termogravimetrie. Bylo prokázáno, že nízké koncentrace huminových kyselin způsobily zvýšení stability zkoumaného PVA. Naopak, vyšší koncentrace měly pouze slabý stabilizační efekt a v některých případech přítomnost huminových kyselin vedla dokonce k destabilizaci PVA. V další části byla upravena životnost polymerního materiálu pomocí gama záření. Získané výsledky naznačovaly, že přítomnost amonných a sodných solí způsobila značnou stabilizaci polymeru ve srovnání s čistým PVA a dokonce ukazovaly stabilizační efekt i po dlouhodobé expozici gama záření. Posledním úkolem bylo zhodnotit efekt stárnutí na směsi PVA a huminových kyselin popřípadě jejich solí. Žádné další chemické reakce v těchto směsích nebyly zaznamenány, tudíž možno konstatovat, že připravený materiál vykazoval konstantní fyzikální vlastnosti během celého, několika měsíčního experimentu.

KEYWORDS

humic acids, antioxidants, thermal analysis

KLÍČOVÁ SLOVA

huminové kyseliny, antioxidanty, termická analýza

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DECLARATION

I declare that this thesis has been compiled by myself and on my own and I cited all my information sources completely and correctly. The diploma thesis is in terms of its contents a property of the BUT Faculty of Chemistry and its usage for commercial purposes is subject to a prior consent of the supervisor and the dean.

PROHLÁŠENÍ

Prohlašuji, že jsem diplomovou práci vypracovala samostatně, a že všechny použité literární zdroje jsem správně a úplně citovala. Diplomová práce je z hlediska obsahu majetkem Fakulty chemické VUT v Brně a může být využita ke komerčním účelům jen se souhlasem vedoucího diplomové práce a děkana FCH VUT.

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signature of diploma thesis author
podpis diplomanta

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CONTENTS

1. INTRODUCTION

Synthetic polymers are essential for modern human life, since they are used in industrial and agricultural fields. However, most synthetic polymers that have been developed by using petroleum and coal as raw materials are not compatible with environment, since they cannot be included in the natural recycling system. There are serious contraindications between the convenience that people require today and compatibility with natural environment. We lose all the convenient features and materials which science has developed through human history. Therefore, research on the environmentally compatible polymers (green polymers) is the key to sustainable development that can maintain our rich and convenient life [1].

In order to develop green polymers, it is essential to understand that nature construct a variety of materials that can be used. Saccharides have already been used extensively in the food, medical and cosmetic industries. Plant material such as cellulose, hemicellulose and lignin are the largest organic resources [1]. Lignin is usually considered as a polyphenolic material having an amorphous structure; it is nontoxic and extremely versatile in performance. Lignin is one of the most important precursors of coals formation determining their unique chemical composition. In its structure the original lignin structure can be identified. Other plant-origin and components such as lipids are also present in a relatively high abundance. Such mixture gained and unique and complicated structure which has a high technological potential [2].

The thermal resistance is one of the most dominative properties for polymer materials, as it ultimately governs the mechanical properties, durability, spectral stability and life cycle of polymers [3]. The combination of heat as the energy and oxygen as the reactant is a major factor in material degradation. Thermal and oxidation stability of a polymer material is an important physico-chemical property, which can restrict or enlarge the application area of a product [4]. Material behavior may be modified by the addition of compounds acting as antioxidants. Antioxidants are substances that when present in low concentrations with those of an oxidisable substrate, significantly retard oxidation of that substrate. Over the last years here is a tendency to substitute synthetic additives by natural ones, for example cellulose, lignins etc. Recently there appeared the possibility to use lignite, the low-rank coal, as an antioxidant that contains lignin-derived compounds, i.e., polyphenols, known to have a significant antioxidant property.

2. STATE OF THE ART

2.1 Degradation of polymers

Thermal and oxidation stability of a polymer material is an important physico-chemical property, which can restrict or enlarge the application areas of a product. The combination of oxygen as the reactant and heat as energy source is a major factor in material degradation. In most cases, the oxidation processes occurring in the condense phase exhibit induction period (IP) where seemingly no chemical reaction takes place. At the end of induction period, also a sudden change in materials characteristics mostly takes place so that the length of induction period is often considered as a relative measure of material stability [4].

2.1.1 Oxidation of polymers

Most organic compounds are oxidized by atmospheric oxygen at moderate temperatures (< 200 °C). This is because they can undergo *autooxidation*, a free radical chain process that involves transient alkylperoxy radicals [5]. This process is characterized by the fact that a rate of oxygen consumption increases in time up to a point at which a maximum rate is attained [6]. Synthetic and natural rubbers are particularly susceptible to atmospheric oxidation because the fundamental units of these polymers contain labile C–H and C=C groups [5]. Bolland and Gee [7] discovered mechanism of thermal oxidation of polymers.

1. Initiation – production of free-radicals (1 and 2)
2. Propagation – formation of hydroxyperoxides (3 and 4)
3. Termination – production of non-radical products (5–7)

$$PH \longrightarrow P^{\bullet} + H^{\bullet} \quad (1)$$

$$PH + O_2 \longrightarrow P^{\bullet} + HO_2^{\bullet} \quad (2)$$

$$P^{\bullet} + O_2 \longrightarrow PO_2^{\bullet} \quad (3)$$

$$PO_2^{\bullet} + PH \longrightarrow POOH + P^{\bullet} \quad (4)$$

$$PO_2^{\bullet} + PO_2^{\bullet} \longrightarrow \text{Non-radicals products} + O_2 \quad (5)$$

$$P^{\bullet} + PO_2^{\bullet} \longrightarrow POOP \quad (6)$$

$$P^{\bullet} + P^{\bullet} \longrightarrow P - P, \quad (7)$$

where PH represents hydrocarbon, $P^{\bullet}$ is an alkyl radical produced by removal of a hydrogen atom from PH, and $PO_2^{\bullet}$ is the alkyl peroxy radical formed by reaction of $P^{\bullet}$ with molecular oxygen. The high temperature and shearing stresses required for compounding, extrusion, and molding of polymeric materials, can produce alkyl radicals by homolytic chain cleavage. Oxidatively sensitive substrates can react directly with oxygen, particularly at elevated temperatures, to yield radicals. Propagation reactions can be repeated many times before conversion of an alkyl or peroxy radical to non-radical species [8].

2.1.2 The gamma radiation effect on polymers

Polymer products undergo degradation, which is mainly caused by oxygen, ozone, heat and dynamic stress. Radiation is also responsible for the polymer degradation, oligomer formation and chain cross-linking. Understanding γ-radiation-oxidation process is important, since

polymers, when irradiated, are mostly exposed also to air during and/or after irradiation. Radiation doses applied in practice are usually in the range of several tens of kGy [9].

2.2 PVA

Polyvinyl alcohol (PVA) is a water soluble high-molecular compound, not soluble in ordinary organic solvents. It is a white solid in the form of flakes, with excellent tensile stress, mouldability, impact strength, wear resistance and excellent electrical insulation. Polyvinyl alcohol is the most widely produced water soluble and biodegradable synthetic polymer worldwide. It is easily esterified or etherified and undergoes many other reactions whose behavior resembles that of molecular alcohols. Its water solubility is related to the degree of hydrolysis and of polymerization, with a maximum at 88% hydrolysis and higher solubility for lower degrees of polymerization [10].

2.2.1 Manufacture of PVA

The primary raw material used in the manufacture of polyvinyl alcohol is vinyl acetate monomer. It is manufactured by the polymerization of vinyl acetate followed by partial hydrolysis. The process of hydrolysis is based on the partial replacement of ester group in vinyl acetate with the hydroxyl group, and is completed in the presence of aqueous sodium hydroxide, following gradual addition of the aqueous saponification agent. Polyvinyl alcohol is precipitated, washed and dried. The degree of hydrolysis is determined by the time point at which the saponification reaction is stopped.

2.2.2 Degradation of PVA

PVA is known to be a truly biodegradable synthetic polymer since the early 1930s, and many efforts have been carried out to isolate PVA-degrading microorganisms. The major biodegradation mechanism of PVA is represented by the random endocleavage of the polymer chains. The initial step is the specific oxidation of 1,3-hydroxyl groups, mediated by oxidase and dehydrogenase type enzymes, resulting in β-hydroxylketone as well as 1,3-diketone moieties. The latter groups are susceptible to carbonecarbon bond cleavage promoted by specific β-diketone hydrolase, giving rise to the formation of carboxyl and methyl ketone end groups [11]. However, PVA degradation in aqueous and soil environments has proved quite slow degradation under unadapted conditions. Blends of PVA with natural polymers such as starch, chitin, chitosan, sugar cane bagasse and other lignocellulosic fillers have been extensively studied in order to confer greater hydrophilicity and accelerate degradation while simultaneously reducing production costs [12].

Fourier transform infrared (FTIR) spectroscopy was used to investigate the molecular mechanisms of the degradation process in conjunction with thermogravimetric analysis (TG). Degradation of PVA in an inert atmosphere was demonstrated to be a two-step process by differential of mass loss curve (DTG). The first step in the mass loss curve results from the elimination of water. In the second step, in the inert atmosphere, pyrolisation occurs producing some organic volatiles. The pyrolisation process also leaves a large residue of carbonaceous material, which was observed to be oxidisable at 1000 °C in air leaving no measurable ash content. The degradation process in the air atmosphere showed some

significant differences from that of the inert environment. The first step showed a much reduced rate of mass loss indicating the inclusion of oxygen in the polymer. The second step of the degradation process in air was also observed to differ from the inert environment, while two mass loss steps were observed with maximum rates at 378 and 449 °C [13]. In both atmospheres a residue was observed at 600 °C. While for the inert atmosphere the residue was larger and expected, a small residue persisted in the air environment too.

The FTIR spectra for the degradation of PVA in nitrogen and air atmosphere showed a marked reduction in the intensities of all the absorption bands in the PVA spectrum as the degradation process proceeded. The new bands at 1715 and 1595 cm^{-1}, attributed to carbonyl (C=O) and carbon–carbon double bond (C=C) stretching, respectively, were also evident particularly in the air atmosphere and to a lesser extent in the inert atmosphere.

For the degradation in nitrogen, both the hydroxyl O–H and the C–H stretching modes reduced sharply in intensity with an onset at approximately 220 °C and a maximum rate at approximately 240 °C [13]. The decline in the intensities of both of these modes correlated extremely well with the mass loss curve for the inert environment. The sharp decline in the intensity of the O–H peak was indicative of the mechanisms for elimination of water as the first step of the degradation process. The O–H peak declined to zero intensity by the end of the first step indicating that complete elimination of the alcohol groups occurred. The product of the elimination was olefinic resulting in the production of C=C in the polymer residue.

The degradation of PVA in an air atmosphere produced a similar reduction intensity of the O–H and the C–H stretching modes. The decline in the intensities of these modes compared well with the mass loss as a steady decline in the intensities of each mode was observed. The reduction in intensity of the O–H stretching mode correlated well with the first step of the degradation process indicating that elimination might be an important mechanism in the first step. A number of mechanisms could therefore be attributed to the decline in the O–H peak particularly as it was delayed to much higher temperatures than was the case for degradation in an inert atmosphere.

A large carbonyl peak around 1595 cm^{-1} appeared in the spectrum and was observed to coincide with the first degradation step of the mass loss curves. This was indicative of the inclusion of atmospheric oxygen in the polymer. This peak had a center of mass at about 250 °C and corresponds with the maximum rate of degradation in the first step in TG experiments [13]. The carbonyl peak remained important in the degradation throughout the first degradation step and diminished towards the end of this step.

2.3 Antioxidants

Antioxidants are used to retard the reaction of organic materials, such as synthetic polymers, with atmospheric oxygen. This reaction can cause degradation of the mechanical, aesthetic and electrical properties of polymer. The need for antioxidant depends upon the chemical composition of the substrate and the conditions of exposure. Relatively high concentrations of antioxidants are used to stabilize polymers such as natural rubber [8].

There are two types of antioxidants:

1. Primary antioxidants, which delay or inhibit the initiation step and interrupt the propagation step of the radical chain reaction. Antioxidants act by transferring a hydrogen atom to the peroxy radical. The resulting radicals from the oxidized antioxidant are stabilized by resonance and are relatively unreactive and therefore are not capable of initiating or propagating the oxidative reaction.
2. Secondary antioxidants are peroxides decomposers. These compounds are for instance thioesters and phosphites.

Primary antioxidants (AH), such as hindered phenols and secondary aromatic amines, inhibit oxidation by competing with the organic substrate (PH) for peroxy radicals. This shortens the kinetic chain of the propagation reactions.

$$PO_2^{\bullet} + AH \xrightarrow{k_1} POOH + A^{\bullet} \quad (8)$$

$$PO_2^{\bullet} + PH \xrightarrow{k_2} POOH + P^{\bullet}. \quad (9)$$

Because k_1 is much larger than k_2, hydrogen-donating antioxidants generally can be used at low concentration. The usual concentration in saturated thermoplastic polymers ranges from 0.01 to 0.05 %, based on the weight of polymer. Higher concentration (0.5–2 %), are required in substrate that are highly sensitive to oxidation, such as unsaturated elastomers.

Hindered phenols contain hindered hydroxyl group with at least one bulky alkyl group in the ortho position. This is necessary for high antioxidant activity. Steric hindrance decreases the ability of a phenoxyl radical to attack a substrate and thus produce an alkyl radical. The use-fullness of a hindered phenol for a specific application depends on its radical-trapping ability, its solubility in substrate, and its volatility under test conditions [8].

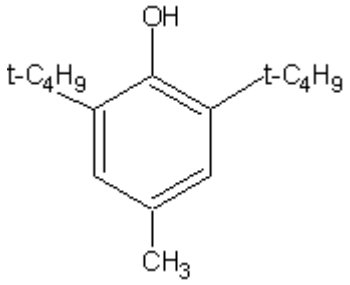

Figure 1 *2,6-Di-tert-butyl-p-cresol*

Aromatic amines are other class of highly effective peroxy radical scavengers. They are more effective than phenolic antioxidant for the stabilization of easily oxidized organic materials, such as unsaturated elastomers and protect them against ozone degradation. But they have a tendency to form highly colored polyconjugated systems.

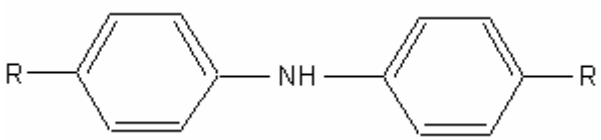

Figure 2 *Alkylated diphenylamines*

Antioxidants provide stability of polymers by quenching free radicals and decomposing hydroxyperoxides. Other important parameters are [14]:

- Volatility – antioxidant, as well as its transformation product that may provide stability, does not volatilize from the stabilized compound.
- Solubility – should be soluble in the stabilized compound. If they are not soluble, they should at least migrate on a surface or diffuse slowly.
- Color stability – does not provide unwanted color because of the transformation chemistries associated with preventing oxidation.
- Cannot cause corrosion
- Without toxicity, odor – for application that involve food contact, home or personal use, these parameters are key issues.

2.3.1 Efficiency of antioxidants in polymers

Nearly all polymeric materials require the addition of antioxidants to retain physical properties such as mobility, solubility and volatility and to ensure an adequate service life [8]. It has been recognized that the migration of stabilizer molecules in a polymer matrix can make a significant contribution to the protection time of the stabilizer. There are three parameters that determine the protection time of a stabilizer:

1. The physical loss of the stabilizer due to evaporation, leaching or blooming. Highly mobile antioxidants not only diffuse rapidly towards the oxidation site and react fast with the radicals, but also diffuse easily towards the surface and leave polymers without being active. There are two phenomena that determine the decrease of the antioxidant concentration in a polymer: (a) the diffusion towards the surface and (b) reaction of an antioxidant with the available radicals.
2. Chemical loss of the stabilizer due to the reaction with the radical.
3. The minimum concentration, at which the stabilizer is still active, can be called the critical stabilizer concentration [15].

2.3.1.1 Effective temperatures for antioxidant

Certain types of antioxidants provide free radicals scavenging capability, although over different temperature ranges. Hindered phenols are capable to provide long-term thermal stability below the melting point of the polymer as well as melt processing above the melting point of the polymer. Most hindered phenols are used across the entire temperature range. Thiosynergists, in combination with a hindered phenol, contribute long-term thermal stability below the melting point of polymer. Hindered amines, useful for UV stabilization, are also useful for long-term thermal stability below melting point of the polymer. They are ineffective at temperature higher than 150 °C. Phosphites, hydroxylamines, and lactones are most effective during melt processing. They are not effective as long-term thermal stabilizers.

One anomaly is the hindered phenols based on tocopherols. Even though tocopherols, such as vitamin E, fall into general class of hindered phenols, they behave more as melt-processing stabilizers, and less as reagents for providing long-term thermal stability [8].

2.3.1.2 Antioxidant blends

In practical application there is often use more than one type of antioxidants. A mixture of antioxidants that function by different mechanism might be synergistic and provide higher degree of protection than the sum of the stabilizing activities of each component work as a synergist. The most frequently used synergistic mixtures are combinations of radical scavengers and hydroxyperoxides decomposers. Mixtures of antioxidants can also work as antagonist. They involve relatively strong acids and bases that can react with antioxidants and divert them. They become without stabilization effect [8].

2.3.2 Lignite as a source of energy

Coal is a nonrenewable energy source. The energy in coal comes from the energy stored by plants that lived hundreds of millions of years ago, when the earth was partly covered with swampy forests. For millions of years, layers of water and dirt, trapping the energy of the dead plants, covered a layer of dead plants at the bottom of the swamps. The heat and pressure from the top layers turned the plant remains into coal.

The organic structure of coal can be regarded as consisting of heterogeneous aromatic structures, with aromaticity increasing from low rank (lignite, xylite) to high rank coal (semi-anthracite and anthracite).

Table 1 *Elemental composition of selected firing* [16].

	C (%)	**H (%)**	**O (%)**	**N (%)**
Wood	50.0	6.0	43.8	0.2
Peat	57.0	6.0	35.0	2.0
Lignite	65.5	5.5	28.0	1.0
Brown coal	73.0	6.0	19.8	1.2
Gas coal	85.8	5.5	7.0	1.7
Anthracite	94.0	2.4	1.9	1.2

It is a general concept that lignite has been known as fuel and source of energy just like the other kinds of coal mine [17]. Because of its low energy density, brown coal (i.e. lignite) is inefficient to transport and is not traded extensively on the world market compared with higher coal grades. It is often burned in power stations constructed very close to any mines. Lignite belongs to group of low rank caustobiolities. It has a unique composition since it represents an intermediate substrate on the transformation road from parent biomass to the dehydrated, dehydrogenated and deoxidized carbon-type complex. It is a very complicated mixture of low and high molecular weight organic compounds—complex of cyclic-aromatic-aliphatic hydrocarbons and their derivates [18]. In the Czech Republic important source of lignite is a mine Mír, which is located in South Moravia. These lignites contain high percentage of water and ash. Composition of South Moravia lignite shows Table 2. Though

this lignite has low energy density it is used as a fuel in Hodonín power station [19]. Lignite should not be viewed as some kind of low quality fuels only but also as a valuable raw material for production of a large variety of special chemicals [20].

Table 2 *Composition of South Moravian lignite* [21]

Matter	**(weight %)**
Water	48.0–50.0
Ash	11.6–13.2
Combustible	39.1–40.3
H	~ 2.2
C	25.9
O	10.9
S	0.8
N	~ 0.3
Halogenides	< 0.01

2.3.3 Humic substances

Humic substances (HS) are natural products of microbial degradation of death plant tissues and animal bodies and represent major pool of lignites [18]. Humification is considered to represent one pathway in formation of humic substances. It is a chemical-microbiological process of transforming from living organism into a general class of refractory organic compounds. It is the second largest process in the world after photosynthesis.

Coalification of plant debris preserved in peat mires leads to the formation of humic coals. The term brown coal is often used for lignite and sub bituminous coals, while hard coal indicates coals of higher rank. The net result of coalification is an extension of the humification process to include a continuous enrichment of fixed carbon with increasing rank [22]. However the vital importance of the oxidized lignite, called leonardite, is a source of readily available humic material. In various respect, the humic material of the lignite is identical with soil humus having essentially the same sources. The soil humus and lignite humus both represent the residually organic material from the past plant generations.

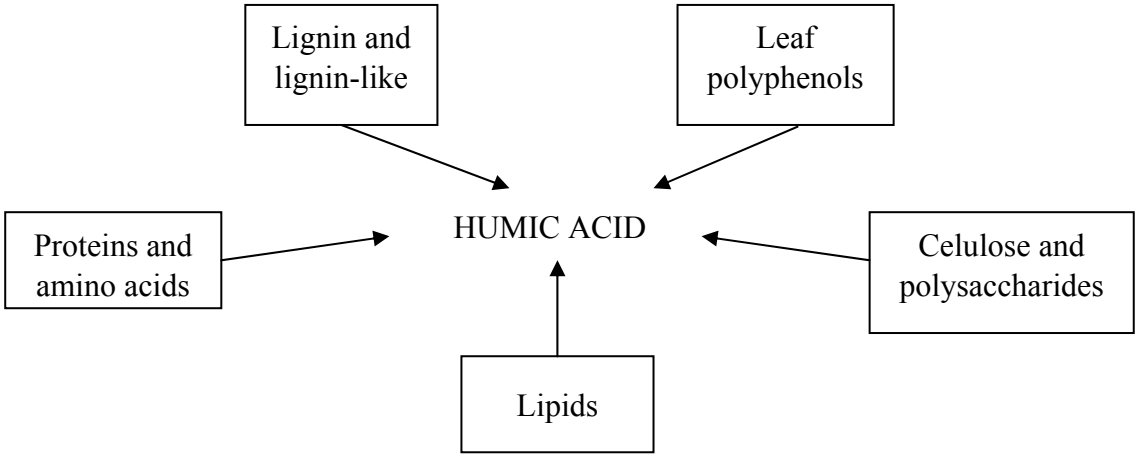

Figure 3 *The major precursors of soil organic matter*

Humic substances, dark colored, heterogeneous organic compounds produced as by-products of microbial metabolisms, are among the most widely distributed organic material on the planet [23]. This assembly contributes vital properties to soil, including sequestration, mobilization, and oxidative or reductive transformation of organic xenobiotic molecules, trace gases, and trace metal contaminants [24]. They cannot be described by unique, chemically defined molecular structures. It is suggested that HS are mixtures of plants and microbial carbohydrates, proteins and lipids with partially degrades lignins and tannins and also including microbial materials such as melanins [23].

2.3.4 Formation of humic substances

Although the biochemistry of the formation process of HS has been studied hard and for a long time, this is still the subject of long-standing and continued research [2]. Several pathways exist for the formation during the decay of plants and animal remains. The classical theory, popularized by Waksman, is that humic substances represent modified lignins but the majority of present-day investigators favor a mechanism involving quinones. One consideration that has not received adequate attention is that, in many given soil, not all humic components may be formed by the same mechanism [23]. Humic acid, for example, may originate from polyphenols of plant or microbial origin whereas fulvic acids may consists of products arising from the condensation of sugars and amines.

The lignin theory

For many years, the view was held that lignin was the source of humic substances. Waksman cited the following evidence in support of the lignin theory of humic acid formation [23].

1. Lignin and humic acid are decomposed with considerable difficulty by the great majority of fungi and bacteria
2. Lignin and humic acid are soluble in alkali, partly soluble in alcohol and pyridine and precipitated by acids.
3. Both are acidic in nature an are able to combine with bases
4. When lignins are warmed with warmed with aqueous alkali, they are transformed into methoxy-containing humic acids.

Conversion of lignin to humic substances:

The most obvious changes in lignin would be a loss of OCH_3 groups, with exposure of phenolic OH groups, and oxidation of terminal side chain to form COOH groups. Demethylation and oxidation of side chains lead to the formation of products enriched in acidic functional groups (COOH and OH) and that have lower C but higher oxygen contents than original lignin. Hatcher and Spiker [25] have advanced a modified degradative model for humification. In their model, resistant plant (lignin, cutin, suberin) and microbial biopolymers are the precursors of humic substances. Increasing degradation leads to the formation of macromolecules that have somewhat similar molecular weights but that are enriched in oxygen-containing functional groups (i.e.: COOH, C=O, OH).

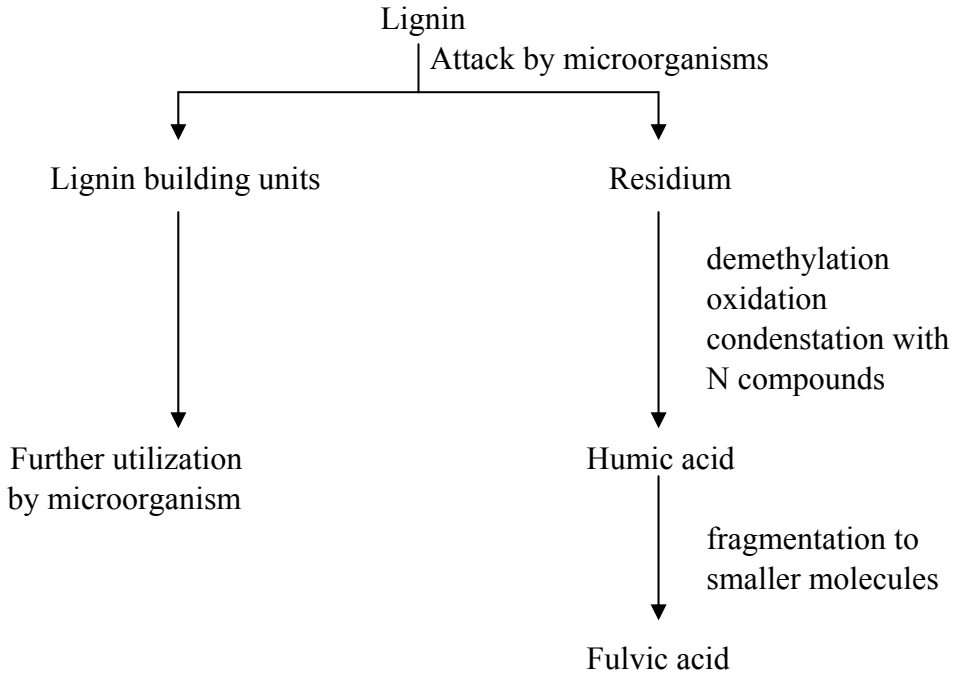

Figure 4 *Schematic representation of the lignin theory of humus formation*

The polyphenol theory

According to current concepts, quinones of lignin origin, together with those synthesized by microorganisms, are the major blocks from which humic substances are formed. The order of formation of humic substances would thereby follow the order: fulvic acid–humic acid–components of humin. The formation of brown-colored substances by reaction involving quinones is a well-known phenomenon [23].

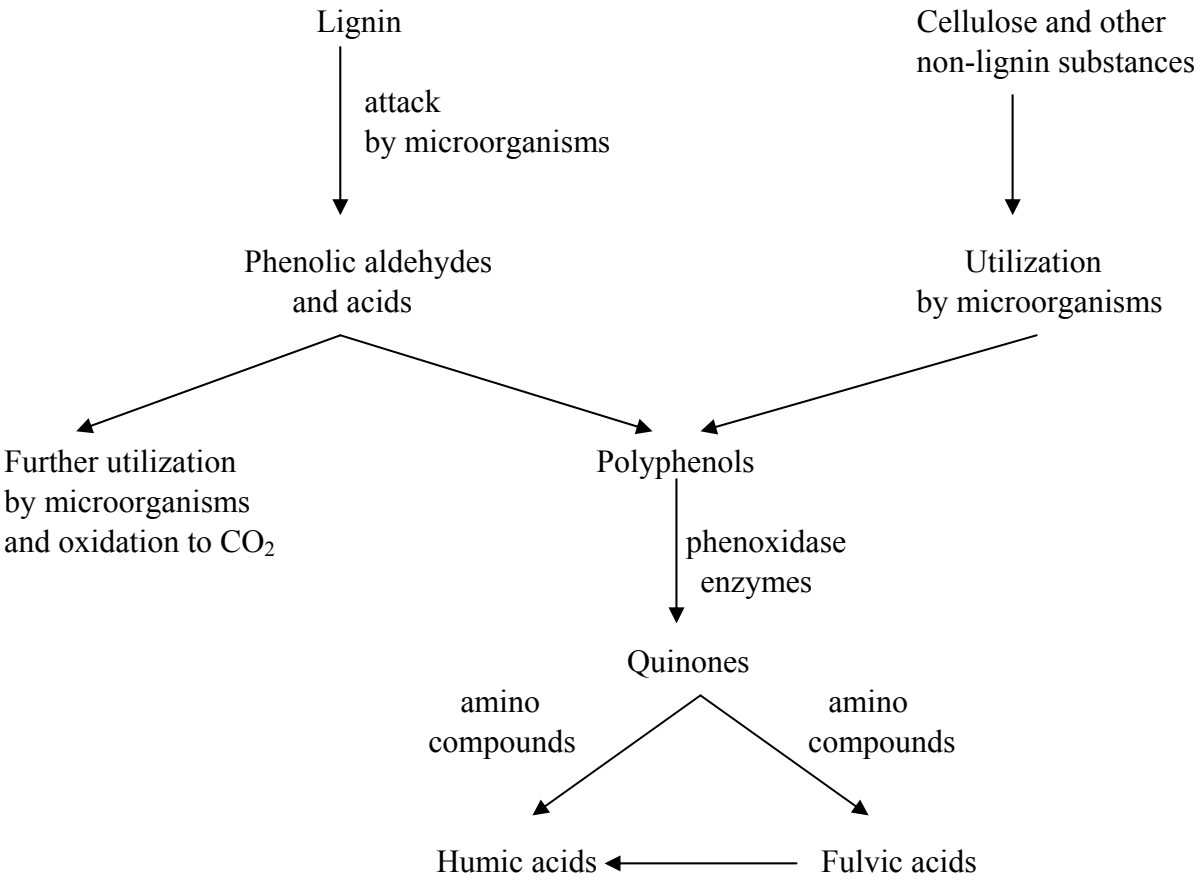

Figure 5 *Schematic representation of the polyphenol theory of humus formation*

According to recently introduced concept, humification in soil can be considered as a two-step process of biodegradation of dead-cells components, aggregation of the degradation products [26]. In light of the supramolecular model, one needs not to invoke the formation of new covalent bonds in the humification process that leads to the production of humus. Humification is the progressive self-association of the mainly hydrophobic molecules that resist the biodegradation. These suprastructures are thermodynamically separated by the water medium and adsorbed on the surfaces of soil minerals and other pre-existing humic aggregates. The exclusion from water means exclusion from microbial degradation and the long-term persistence of humic matter in soil.

2.3.5 Chemical structures identifies in humic substances

HS are a mixture of complex organic compounds that are usually divided into three fractions based on aqueous solubility [27]:

- Humic acid (HA), the fraction of HS that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values.
- Fulvic acid (FA), the fraction of HS that is soluble in water under all pH conditions.
- Humins, the fraction of HS that is not soluble in water at any pH value.

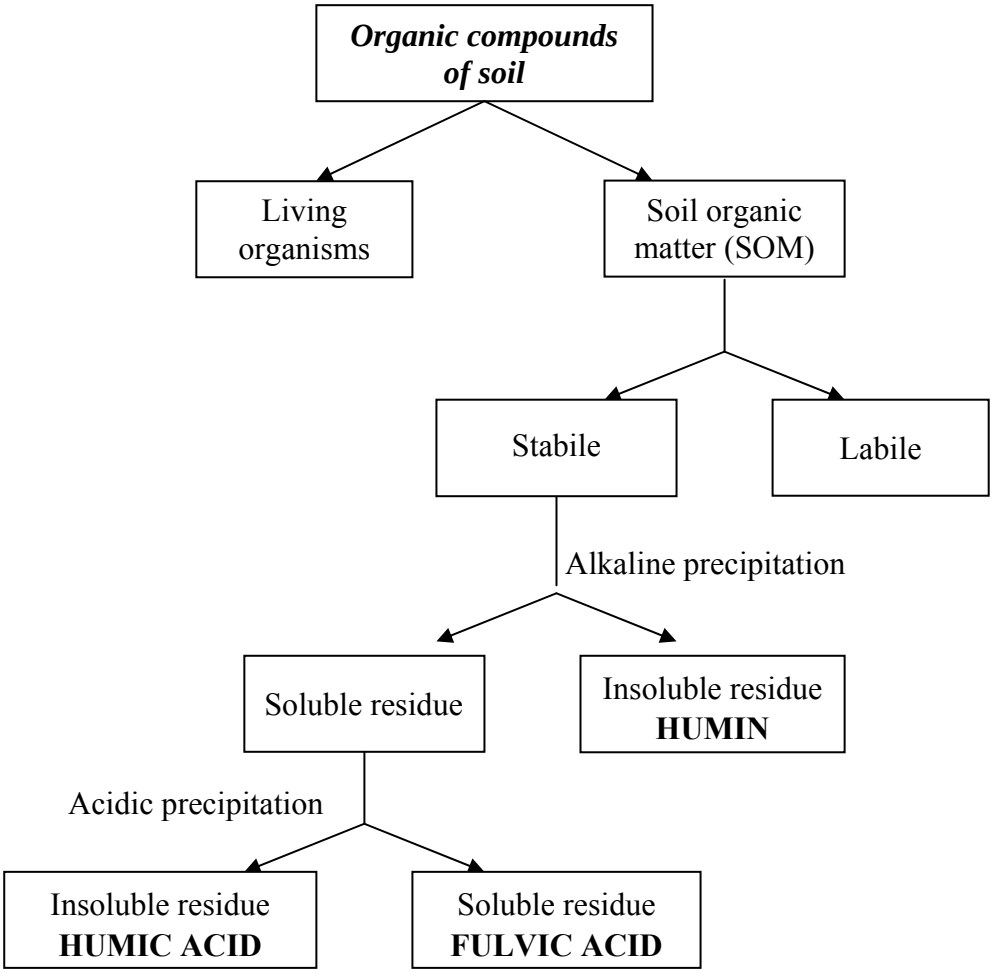

Figure 6 *Scheme of division of humic substances in dependence of their solubility*.

It is known that the chemical composition of humic matter includes aromatic rings that interact with each other and with aliphatic chains, giving rise to macromolecular-like aggregates with different masses. Considering that the genesis of HS can involve combinations of several reaction pathways and wide variety of chemical binding systems, it is very difficult to define a clear concept on their composition. Many of the original classical methods to understand the nature of HS were based on elemental composition, but the results obtained represent averages for agglomerations of molecules and it is impossible to derive precise empirical formulae from these data.

Advanced spectroscopic, pyrolytic, and soft ionization techniques have begun to reveal the makeup of many of the individual fragments of humic material produced through degradation of biomolecules, and to provide information concerning their relative mobilities. There is substantial evidence that lipid-derived molecules or moieties, including branched and linear alkanes, alkenes, fatty acids, dicarboxylic acids, and long chain alcohols/ethers, ketones/aldehydes, and esters, make up a significant portion of HS. These compounds have been identified as major components of humic fractions in numerous pyrolysis studies, especially when methylation via tetramethylammonium hydroxide (TMAH) is used to preserve carboxyl groups. The distribution of alkanes and fatty acids, which favors an even

number of C atoms, indicated microbial or plant origin. While fatty acids were dominant components of the lipid-like portion of the humic matter, smaller amounts of alkyl esters and alcohols/ethers were also observed.

Aromatic fragments observed within humic material may be derived from lignin or other sources. Alkylbenzenes and alkylphenols are detected regularly in the pyrolysates of HS, and can feature alkyl chain lengths of over 25 C atoms. However, many of these alkylaromatic molecules may be artifacts created by secondary reactions. Pyrolysis preceded by methylation indicates benzene tricarboxylic acids are common humic constituents, as does ESI-MS. Simple sugars ribose and glucose have been identified using ESI-MS spectra. These spectra also provided evidence for the existence of polypeptides of up to 10 amino acids in length.

Obviously, organic O is the primary source of reactivity in HS, as functional groups containing O provide polarity. Molar O:C ratios for HA and FA typically fall within 10 % of 0.5 and 0.7, respectively. These different ratios reflect the pH-dependent properties of many O functional groups, given the operational basis for separation of HA and FA [24].

Leenheer [28] noted that a small but significant fraction of humic carboxyl groups possess dissociation constants (pK_{aS}) as low as 0.5. Using NMR spectroscopy and methylation, chemical degradation, and pH gradient fractionation, they demonstrated that these strongly acidic structures are probably polycarboxylic acids located near ether or ester functional groups and surrounded by additional electronegative substituents.

Comparison of HS examined with thermochemolysis–MS, or thermochemical degradation and volatilization using TMAH or tetraethylammonium acetate, as well as those processed using multistep chemical degradations and examined with pyrolysis and NMR spectroscopy, indicated that alkyl molecules containing carboxyl groups exist as free acids loosely associated with other moieties, as tightly trapped molecules within the organic matrix, and as acids linked to the matrix via ester bonds.

However, processing by oxidation or acid boiling can produce structures indicating the interaction of unpaired quinone electrons with neighboring H nuclei, and resembling the spectrum of 2,6-dimethoxy-p-benzosemiquinone. Several 2D NMR studies identify signals from unsaturated ketone groups, consistent with the presence of quinones. Low-temperature fluorescence and ESR studies of a forest soil FA suggested that quinone rings featuring four protons were common, but those structures featuring substitutions were also present. The ESR studies of quinone moieties in HS indicate that the population of this functional group is small, in the range of $10^{16–18}$ spin g^{-1}, and may be divided into stable and transient organic radicals [24].

Kingery [29] presented 2D NMR evidence of ortho- (1,2) and para- (1,4) substituted phenol groups within a soil HA sample. FA tends to contain slightly more phenol groups than HA, and with decreasing apparent molecular size; the proportion of phenols in humic fractions tends to increase.

In summary, modern spectroscopic studies confirm earlier data regarding the variety of oxygenated functional groups contributing to the chemical reactivity of HS. Carboxyls, including unusual alkyl polycarboxyl moieties near ester or ether groups, determine the deprotonation and charge behavior of HS under low pH conditions, while phenols and alcohols play an important buffering role within higher pH solutions. Quinones are not sufficiently numerous to account for the redox behavior of HS. Ester and ether bonds link different portions of humic molecules. Carbohydrate-based functional groups make up a large portion of humic O groups [24].

Early chemical degradation analysis of humic materials suggested that the carbonaceous structural framework or "skeleton," of the component molecules was primarily aromatic. The high proportion of alkyl substituents remaining in HA and humin samples after a multi-step chemical degradation process (ultrasonic disruption in methylene chloride, followed by BF_3 methanol transesterification and HI treatment) suggests that these structures are an integral part of the humic C skeleton [24].

2.3.6 Humic acid

Humic acid (HA), one of the most important components of HS, help break up clay and compacted soils assist in transferring micronutrients from soil to plants, enhance water retention, increase seed germination rates, and stimulate the development of micro flora populations in soil [2]. The lignite HA has been especially interesting in respect to e.g., structural chemistry and different technical applications. The HA content is usually the highest in naturally oxidized lignite derivatives, and thus several processes have been developed to synthetically oxidize other common low rank coals with a view to increase the content of oxygenated functional groups (–COOH, –CO, –CO–O–C–, –OH, etc.) which makes these components soluble in alkaline conditions. Nowadays, structural viewpoint is based on the fact that HA-type materials are composed of several hundreds of organic constituents, which can be classified into different main categories such as carbohydrates, and their nitrogen-containing derivates, polypeptides and proteins, and aliphatic and aromatic hydrocarbons with phenolic, carboxylic and methoxy functionalities [30].

2.3.6.1 Reactive functional groups

Elemental contents

The major elements in humic and fulvic acid are carbon and oxygen. The carbon content of humic acids in soil is generally considered to ranges from 53.8 to 58.7 percent; oxygen content varies from 32.8 to 38.3 percent. Fulvic acids have lower carbon but higher oxygen contents. Percentages of hydrogen, nitrogen and sulfur vary from 3.2 to 7.0, 0.8 to 4.3 and 0.1 to 3.6 percent, respectively [23]. Disregarding sulfur, the average chemical formula for humic acid would be $C_{10}H_{12}O_5N$. For fulvic acid, the formula would be $C_{12}H_{12}O_9N$.

Table 3 *Usual range for the elemental composition of humic substances* [23].

Element	Humic acid	Fulvic acid
Carbon	53.8–58.7 %	40.7–50.6 %
Oxygen	32.8–38.3	39.7–49.8
Hydrogen	3.2–6.2	3.8–7.0
Nitrogen	0.8–4.3	0.9–3.3
Sulfur	0.1–1.5	0.1–3.6

Because of lack of specificity, absolute values concerning of relative distribution of functional groups in humic substances must be accepted with reservation. For instance, based on wet-chemical methods, as a result of the variability in reactivity of OH groups, values reported for "phenolic OH" and "alcoholic OH" can be somewhat misleading. In general, it can be pointed out, that COOH and C=O groups increase in amount during humification while alcoholic OH, phenolic OH and OCH_3 decrease [23].

FA contains more functional groups of an acidic nature, particulary –COOH. The total acidities of FA (900–1400 mmol/100 g) are considerably higher than for HA (400–870 mmol/100 g). Another important difference is that while the oxygen in FA is largely in known functional groups (–COOH, –OH, –C=O), with high oxygen content, the acidity and degree of polymerisation all change systematically with increasing molecular weight. The proportion of oxygen in HA seems to occur as a structural component of the nucleus [2]. Functional carboxyl and hydroxyl groups in HS were found to be related to biological activity [31] but the manner in which they act has still to be elucidated. Low molecular weight components of HS have proved to be biologically active although high molecular weight components appeared to be similarly active [32].

The reactivity of HA is due in large measure to their high content of oxygen-containing functional groups, including COOH, phenolic-and/or enolic-OH, alcoholic OH, and the C=O of quinones, hydroxyquinones, and possibly α, β-unsaturated ketones. (Poly) phenolic and carboxylic functional groups as one of main constituents of HA chemical structures are supposed to be responsible for their antioxidant effect.

2.3.7 Regenerated humic acid

2.3.7.1 The oxidative depolymerization of coal

Coal is the final result of a diagenetic process which starts from low molecular weight substances like humic and fulvic acids, leads through the loss of functional groups and condensation reactions to the formation of an insoluble tridimensional network [33]. When a hypothetical coal structure as that proposed by Wiser [34] for a medium rank coal is considered, some "weak" points can be identified, who's breaking off and conversion could lead to the "depolymerization" of the original structure and to the production of a substrate (oxycoal) easily convertible in smaller, soluble fragments (HA). This transformation can be achieved through the oxidation reaction, which could ideally be considered as an inverse diagenetic process able to regenerate the molecules, which originally led to the insoluble structure of the coal. The HA produced is generally called "regenerated" humic acid (RHA) or oxyhumic acid [35].

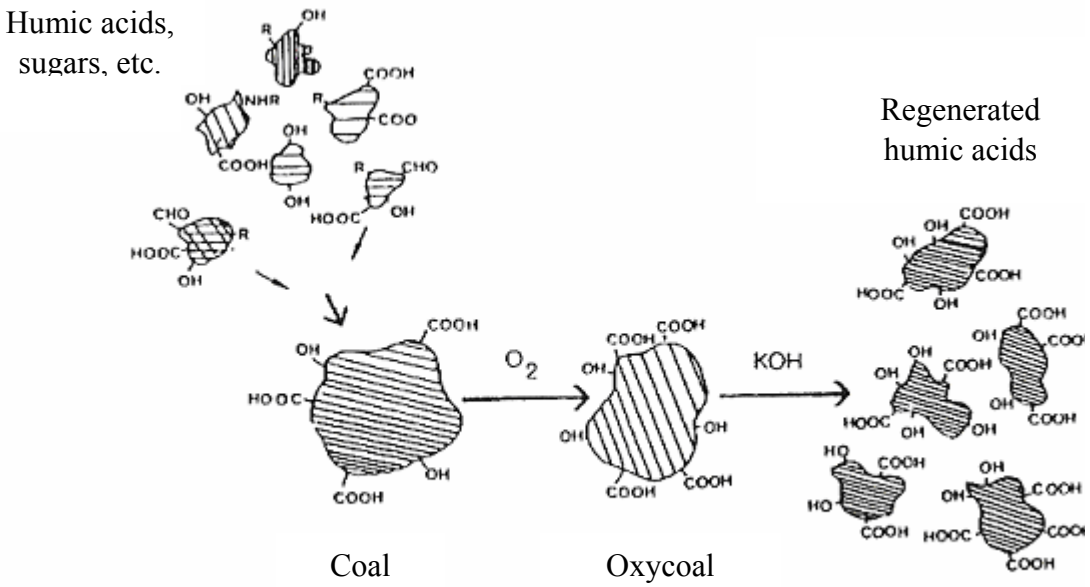

Figure 7 *Coal oxidation as an ideal inverse diagenetic process*

As mentioned before the transformation of coal into HA can be achieved by means of the oxidation process. Oxidation can be performed using many of the oxidants usually utilized in organic chemistry (HNO_3, $KMnO_4$, H_2O_2, etc.). However in this case a good part of the carbon originally presents in the coal (30–40 %) is lost as CO and CO_2. Moreover, with certain reagents (e.g. HNO_3) some extra side-reactions as nitration are involved. Conversely using oxygen or air as oxidants, the fragmentation reaction can be controlled, carbon losses can be minimized (CO and CO_2 evolved in the optimum conditions never exceed 10 %) and almost any coal can be converted in high yields into humic acids [36].

2.3.7.2 The chemical and physical characteristic

The practical final result of the acidic treatment of the alkaline solution of humates, extracted from oxycoal, is a black, amorphous, water-insoluble RHA powder. RHA have similar characteristics and chemical behavior like the original HA, whose conversion led to coal. They are a water insoluble, black amorphous solid. Their solubility is pH dependent and the dissolution of their molecular structure at high pH is related to the presence of many acidic functional groups. The major elements in RHA are carbon and oxygen and their elemental composition (weight percent) would typically vary between the following ranges: C = 60–70 %, O = 23–38 %, H = 3–4 %, N = 1–2 %, S = 0.3–5 %. In fact RHA generally contain more carbon and less oxygen than HA obtained from natural environments. The major functional groups in RHA are carboxylic and phenolic groups.

The molecular structure of RHA is similar like structure of their analogous natural products. The average molecular weights of RHA (Mn, Mw) obtained via HPSEC are generally of the same order of those found for natural HA, by GPC with Sephedex. Mn and Mw values depend on the nature of the coal and on the experimental condition [35].

2.4 Thermal analysis

Thermal analysis is the analytical technique that establishes the experimental data for the variables of state [37]. The term thermal analysis (TA) is frequently used to describe analytical experimental techniques, which investigate the behavior of a sample as a function of temperature. TA is widely employed in both scientific and industrial domains [38]. The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defines thermal analysis as a group of techniques in which a property of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed. The program may involve heating or cooling at a fixed (or variable) rate of temperature change, or holding the temperature constant, or any sequence of these. Since hardly any measurement is worth doing if the temperature is not controlled, almost all measurements are some type of thermal analysis [37].

2.4.1 Characteristics

The advantages of TA can be summarized as follows:

- The sample can be studied over a wide temperature ranges using various temperature programmes.
- Almost any physical form of sample (solid, liquid or gel) can be accommodated using a variety of sample vessels or attachments.
- A small amount of sample is required; the atmosphere in the vicinity of the sample can be standardized.
- The time required to complete experiment ranges from several minutes to several hours.
- TA instruments are reasonably priced [38].

2.4.2 Conformation of thermal analysis instruments

The sample, contained in a suitable pan or crucible, is placed in a furnace and subjected to some desired temperature program. During this procedure, one or more properties of the sample are monitored by use of suitable transducers for converting the properties to electrical quantities such as voltage or current. Measurements are usually continuous and the heating rate is linear with time (but not necessarily). The results of such measurements are thermal analysis curves and the features of these curves (peaks, discontinuitics, changes of slope, etc.) are related to thermal events in the sample [39].

Table 4 *The most common forms of TA*

Property	TA method	Abbreviation
Mass	Thermogravimetry	TG
Difference temperature	Differential thermal analysis	DTA
Alternating temperature	Alternating current calorimetry	ACC
Enthalpy	Differential scanning calorimetry	DSC
Length, volume	Dilatometry	
Deformation	Thermomechanical analysis	TMA
	Dynamic mechanical analysis	DMA
Electric current	Thermostimulated current	TSC
Luminescence	Thermoluminescence	TL

2.4.3 Sample vessels

Sample vessels are commercially available in various shapes made from a range of materials, including aluminum, carbon, gold, platinum, silver and stainless steel. Samples which evolve volatile components, sublime or decompose should be measured using an open-type sample vessels. The mass of commercially available sample vessels ranges from 10 to 300 mg. Gold and platinum should be used for high-temperature measurements. Liquids, gels, biomaterials and other materials likely to produce volatile components should be measured using hermetically sealed sample vessels [38].

2.4.4 Thermogravimetry

Thermal analysis technique to measure mass as a function of temperature and time is Thermogravimetry (TG) [37]. Measurements of changes in sample mass with temperature are made using a thermobalance. A thermobalance is a combination of a suitable electronic microbalance with a furnace, a temperature programmer and computer [39]. TG is used to characterize the decomposition and thermal stability of materials under a variety of conditions and to examine the kinetics of the physico-chemical processes occurring in the sample. The mass change characteristics of a material are strongly dependent on the experimental conditions employed. Factors such as sample mass, volume and physical form, the shape and the nature of the sample holder, the nature and pressure of the atmosphere in the sample chamber and the scanning rate all have important influences on the characteristics of the recorded TG curve. TG curves are normally plotted with the mass change (Δm) expressed as a percentage on the vertical axis and temperature (T) or time (t) on the horizontal axis [38]. The most frequent use of TG is in determining the material thermal stability, relative volatility and also process kinetics. Coupling of TG and differential thermal analysis (DTA) enables some other characteristics to be measured and assessed, for example temperatures of first and second order phase transitions, namely changes of crystal modification, melting, sublimation, boiling, or glass transition [40].

2.5 Reaction kinetics

The combination of oxygen as the reactant and heat as the energy source is a major factor in material degradation. The oxidation processes occurring in the condense phase are very often unknown or too complicated to be characterized by a simple kinetic model. They tend to occur in multiple steps that have different rates. To describe their kinetics, the methods based on the single-step approximation are often used [41].

2.5.1 Single-step approximation

The rate of the processes in condensed phase is a function of temperature and conversion:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \Phi(T,\alpha). \tag{10}$$

The single-step kinetics approximation employs the assumption that the function Φ in Eq. (10) can be expressed as a product of two separable functions independent of each other, the first one, $k(T)$, depending solely on temperature T and the other one, $f(\alpha)$, depending solely on the conversion of the process, α:

$$\Phi(T,\alpha) = k(T)f(\alpha). \tag{11}$$

Combining Eqs (10) and (11), the rate of the complex multi-step condensed-state process can be formally described as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha). \tag{12}$$

The temperature function $k(T)$ in Eq. (12) is mostly considered to be the rate constant and the conversion function $f(\alpha)$ is considered to reflect the mechanism of the process. Equation (12) resembles a single step kinetics equation, even though it is a representation of the kinetics of a complex condensed-phase process. The single-step kinetics approximation thus resides in substituting a generally complex set of kinetic equations by the sole single-step kinetics equation. Equation (12) represents a mathematical formulation of the single-step kinetics approximation [41].

It was discussed that this interpretation of these functions may be incorrect. Since Eq. (12) is a mathematical formulation of the single-step approximation, the functions $k(T)$ and $f(\alpha)$ represent, in general, just the temperature and conversion components of the kinetic hypersurface. The kinetic hypersurface is a dependence of conversion as a function of time and temperature [41]. With only for few exceptions, the temperature function is expressed by the Arrhenius equation:

$$k(T) = A\exp\left[-\frac{E}{RT}\right], \tag{13}$$

where A and E are considered the preexponential factor and the activation energy, respectively, T is the absolute temperature and R stands for the gas constant. It has been justified that, since $k(T)$ is not the rate constant, there is no reason to be confined to the Arrhenius relationship and use of two non-Arrhenius temperature functions was suggested:

$$k(T) = AT^m \tag{14}$$

$$k(T) = Ae^{DT}, \tag{15}$$

where m and D are parameters. A great advantage of the application of Eqs (14) and (15) is that, in contrary to Eq. (13), the temperature integral can be expressed in a closed form. Unlike the temperature functions, there is a wide range of conversion functions applied [42].

2.5.2 Isoconversional methods:

The isoconversional methods represent probably the most widely employed category of methods based on Eq. (12). Their basic idea is that the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion. Under these conditions, the value of conversion function $f(\alpha)$ in Eq. (12) is constant and the reaction rate is a function of temperature only. These methods are often called the model-free methods [43]. The isoconversional methods may be best known through their most popular representatives, the methods of Friedman, Ozawa, and Flynn, Wall and recently also Šimon. Interestingly, all three methods were conceived by the researchers working on the thermal degradation of polymers and since then they have been mostly used in polymer kinetics studies [44].

The principal idea of the isoconversional method is very simple; there are only two basic assumptions:
(I) Rate of the processes in the condensed state is generally a function of temperature and conversion, Eqs (10)–(12). The main implication of Eq. (12) is that the conversion function $f(\alpha)$ at a fixed value of α holds for any temperature or temperature regime, i.e. the mechanism of the process is solely a function of conversion, not a function of temperature.
(II) The activation parameters are obtained from a set of kinetic runs from the dependences of time *vs*. temperature (for isothermal measurements), temperature *vs*. heating rate (for integral and incremental methods with linear heating rate) or from reaction rate *vs*. temperature (for the differential Friedman method). The evaluation is carried out at fixed conversion [43].

2.5.2.1 Isothermal Isoconversional methods

For isothermal conditions, the rate constant is a constant. After separation of variables, Eq. (12) can be rearranged into the form:

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = k \int_0^{t_\alpha} \mathrm{d}t \,, \tag{16}$$

where t_α is the time at which the conversion α is reached. If we denote the primitive function of the integral at the left side of Eq. (16) as F, one can get:

$$F(\alpha) - F(0) = kt_\alpha \Rightarrow t_\alpha = \frac{F(\alpha) - F(0)}{k} \,. \tag{17}$$

The temperature dependence of the rate constant k is usually expressed by the Arrhenius equation, Eq. (13). Combination of Eqs (13) and (17) gives the expression for the time t:

$$t_\alpha = \frac{1}{A_\alpha \exp[-B_\alpha / T]} , \tag{18}$$

where the activation parameters A and B are given as:

$$A_\alpha = \frac{A}{F(\alpha) - F(0)} \tag{19}$$

$$B_\alpha = \frac{E}{R} \tag{20}$$

The subscript α at A_α, B_α and t_α designates the values related to the fixed value of conversion. Hence, the parameters A_α and B_α can be obtained from a series of isothermal measurements, even by direct treatment using Eq. (18) or from its logarithmic transformation leading to the linear dependence $\ln t_\alpha = f(1/T)$.

2.5.2.2 Isoconversional methods at linear heating

(A) Integral methods
For non-isothermal conditions, combination of Eq. (12) and (13) gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = kf(\alpha) = A \exp\left[-\frac{E}{RT} \right] f(\alpha) \,. \tag{21}$$

After the separation of variables and integration, the latter equation gives the results:

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = A\int_0^{t_\alpha} \exp\left[-\frac{E}{RT}\right]\mathrm{d}t\,. \tag{22}$$

Taking into account (19) and (22) can be rewritten as:

$$1 = A_\alpha \int_0^{t_\alpha} \exp\left[-\frac{B_\alpha}{T}\right]\mathrm{d}t\,. \tag{23}$$

Equation (23) should hold for any temperature regime and enables to calculate the time, which the fixed conversion α is reached. For the linear heating program, the furnace temperature can be expressed as:

$$T_\mathrm{f} = T_0 + \beta t\,, \tag{24}$$

where T_f is the furnace temperature, T_0 is the starting temperature of the measurement and β stands for the heating rat. It is mostly assumed that the temperature of the sample, T, equals that of the furnace ($T = T_\mathrm{f}$). From Eqs (23) and (24) can thus be obtained:

$$\beta = A_\alpha \int_0^{T_\alpha} \exp\left[-\frac{B_\alpha}{T}\right]\mathrm{d}T\,, \tag{25}$$

where T_α is the temperature at which the fixed conversion α is reached. The lower integration limit in Eq. (25) is usually set $T_0 = 0$ K since there is no process observed to occur in the sample at the starting temperature of the experiment. The temperature integral at the right side of Eq. (25) cannot be expressed in a closed form. Using the Doyle and Coats–Redfern approximations for the temperature integral in Eq. (25), the Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS) methods, respectively, can be derived. The kinetic parameters are usually obtained from a set of isoconversional temperatures for various heating rates, from the linearized transformation of Eq. (25):

$$\ln\left(\frac{\beta}{T_\alpha^a}\right) = f\left(\frac{1}{T_\alpha}\right), \tag{26},$$

where $a = 0$ for FWO method and $a = 2$ for KAS method. From Eq. (25) the non-linear isoconversional method can be derived.

(B) Differential method

For the linear temperature program, from Eq. (21) one can obtain:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_\alpha = \left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_\alpha = \left[A_\mathrm{k} f(\alpha)\right]\exp\left[-\frac{E}{RT}\right] = A_\alpha \exp\left[-\frac{B_\alpha}{T_\alpha}\right]\,. \tag{27}$$

Equation (27) after a logarithmic transformation:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_\alpha = \ln A_\alpha - \frac{B_\alpha}{T}\,. \tag{28}$$

From Eq. (28) it follows that the dependence of $\ln(\beta\mathrm{d}\alpha/\mathrm{d}T) = f(1/T)$ should be linear. The method represented by Eq. (28) is named after Friedman.

(C) Incremental method

Since the Friedman method employs instantaneous rate values, it is very sensitive to experimental noise and tends to be numerically unstable. Using incremental methods can obviate this trouble. An incremental integral isoconversional method has been recently

suggested. For the linear heating program, if Eq. (22) is integrated within the conversion increment $\alpha_1 - \alpha_2$, one can arrive at:

$$\beta = \frac{A}{F(\alpha_2) - F(\alpha_1)} \int_{T_1}^{T_2} \exp\left[-\frac{B_\alpha}{T} \right] dT = A_\alpha \int_{T_1}^{T_2} \exp\left[-\frac{B_\alpha}{T} \right] dT \,. \tag{29}$$

In this case, the definition of the parameter A_α is obvious from Eq. (29). Due to the integration, the influence of experimental noise is eliminated to a great extent. For an infinitely small increment, Eq. (29) degenerates into Eq. (27). If it is set $\alpha_1 = 0$ at $T_1 = 0$, Eq. (29) degenerates into Eq. (25). From Eq. (29), the incremental isoconversional method to account for variation in the activation energy can be derived [41].

2.5.3 Kinetic predictions

Predictions are among the most important practical features of kinetic analysis. They are widely used to evaluate the kinetic behavior of materials beyond the temperature regions of experimental measurements. For instance, thermal stability can be estimated as the time to reach a certain extent of conversion at a given temperature. Kinetic predictions of this type can be easily accomplished by using the induction period dependence evaluated by an isoconversional method [43].

2.5.4 Induction period

The induction period (IP) is a stage preceding the main oxidation stage. The processes occurring during IP are “invisible” since they are not registered by the experimental techniques used. There is only one point falling to the IP which is detected by the technique employed, i.e., the end of induction period. The end of IP is determined indirectly as the time/temperature of a sudden increase in the rate of the main oxidation stage, i.e., as the oxidation induction time (OIT) in the case of isothermal measurements and the oxidation onset temperature (OOT) in the case of measurements with linear heating [44]. The rate of degradation processes under application conditions is usually too slow. To estimate the stability of material, a sample is mostly subjected to an accelerated test. The principle goal of studies is to extrapolate kinetic data, obtained from stability test. The prediction of long-term durability by extrapolation is a very difficult task since many fundamental scientific problems in this field remain unsolved. A simple extrapolation from high-temperature data to ambient temperature regularly leads to the estimation of unrealistically long durability. Extrapolation to higher temperatures gives more realistic results. For the determination of the low temperature kinetic parameters, very low heating rates are required. The resulting experiments are, therefore, time consuming, but as the calculated values of the activation parameters produce much more reasonable estimates of the induction period, the application of the method is rewarded with much more realistic estimates of the service life of material applications [45].

3. THE AIM OF THE WORK

The work is devoted to investigate a potential of lignite humic acids of various quality and its salts as antioxidants in polymer materials. Thermo-oxidative degradation of polymers is exothermic process, which is associated with a change of a material weight. Therefore, a method of choice is represented by thermogravimetry. In most cases, the oxidation processes occurring in the condensed phase exhibit an induction period (IP), where apparently no chemical reaction takes place. At the end of IP there is often a sudden change of material characteristic, so the length of IP is considered to be a measure of material stability [4]. Thus the aim of this task was to use such approach and assess the antioxidant efficiency of regenerated humic acids with respect to PVA employing different types of temperature functions. Next part is focused to evaluate the ageing effect in the PVA/humic blends. Finally, in the last part the influence of γ-irradiation on durability of polymer material with a content of humic acids, was tested.

4. EXPERIMENTAL PART

4.1 Polyvinyl alcohol

Polyvinyl alcohol (PVA) 28–99 was chosen because of its homogeneity in functional group, linearity and solubility in water. PVA powder in this work was purchased from Fluka. 2 g of PVA were dissolved in 1 liter of water under temperature 70 °C. Various humic acids were added into this solution to obtain several concentrations.

4.2 Humic acids of different quality

The set of humic acids was obtained from several different sources. Details of chosen HA are given in Table 5. All these samples were mixed with solution of PVA (2 g/l) to obtain, after water evaporation, final concentrations in the polymer 2, 5 and 10 % (w/w).

Table 5 *Samples of humic acids from various sources. HA 41 and Oxyhumolit are humic acids from the same source, only extraction method is different*

Sample	Source	Location
HA 7	Peat	Mine Světlík
HA 22	Lignite	Mine Vávlav, Duchov
HA 41	Lignite	Mine Jiří, Sokolov
HA 43	Lignite	Mine Vršava, Most
HA 44	Lignite	Mine Marie, Sokolov
Oxyhumolit	Lignite	Mine Jiří, Sokolov
Kasikara	Lignite	Van, eastern Turkey
Yarikkaya	Lignite	Afyon, western Turkey

Figure 8 *A) North Bohemian basin (Chomutov part, Most part, Teplice part), B) Sokolov basin*

Other set of humic acids was extracted from modified and non-modified lignite. This line of four humic acids was obtained from South Moravian lignite collected from the Mír mine in the area of Mikulčice, near Hodonín, the Czech Republic. Samples were extracted by the IHSS standard alkaline method with 0.5M NaOH and 0.1M pyrophosphate as specified earlier [23]. Before extraction, each lignite sample, milled and sieved (0.2 mm) was pretreated with different oxidizing agent, details are given in Table 6. First, the samples were soaked for 30 minutes in a solution of the agent, then filtrated and washed with deionized water until agent-free. As a reference, a HA sample was extracted from non-treated lignite.

Table 6 *Samples of regenerated humic acids*

Sample	Pretreatment agent
HA 1	–
RHA 2	5% HNO_3
RHA 3	10% HNO_3
RHA 4	20% HNO_3

4.2.1 γ-irradiation

γ-irradiation treatment was used to decrease the stability of polymer/humic blends. Sodium and ammonium humates were mixed with PVA to obtain final concentrations 0.5, 1, 1.5, 2, 5 and 10 % (w/w). These samples were exposed for 22, 36, 41, 55, 69, 84, 91, 105 and 140 days. As a source of gamma rays ^{60}Co gamma-emitter with dose rate 0.26 $kGy \cdot h^{-1}$ was employed. Thus, corresponding doses to which were the samples exposed were from 127 up to 806 kGy.

4.3 Thermal analysis

TG (TA instruments) with the dynamic air atmosphere was used for testing of polymer/humic blends after γ-irradiation, polymer/humic and polymer/HA (from various sources) blends. The airflow rate was set at 25 ml per minute and the heating rate was 10 K per minute from the room temperature to 600 °C. As a sample holder the open platinum pan was used. Polymer/humic blends were repeatedly measured to identify ageing effect on these samples. Samples were stored in the dessicator over NaOH pellets and measured in a given time period. Polymer/regenerated HA blends were measured at heating rates 0.5, 1, 3, 5, 7, 10 and 15 K per minute. The measurement was carried out from room temperature to 600 °C. Weight of samples was approximately 2 mg. All obtained results were evaluated by means of TA Universal analysis software.

4.4 Mathematical data processing

The thermogravimetric records showed two steps of weight loss, the first one attributable to loss of water, whereas the second one to the degradation of the polymer. The onset of the latter step was used to assess the stability of examined samples. The onset temperature corresponds to the end of induction period and was detected by the extrapolation of inclination of 1st derivative weight curve of the TG curve (DTG) for several temperature rates shown in Figure 9.

Three different temperature functions were used for conversion of nonisothermal parameters (temperatures) to isothermal (times). Briefly:
The rate of the processes in condensed state can be formally described as a function of temperature and conversion expressed in Eq. (12). The main assumption is a separability of these functions. It is also supposed that conversion is constant at several temperatures and heating rates. Except very few exceptions, the temperature dependence of rate constant is exclusively expressed by the Arrhenius equation. Its application for the calculation is expressed in Eq. (30).

$$\beta = \int_0^{T_i} \frac{\mathrm{d}T}{A\exp(B/T)} \tag{30}$$

Since there are doubts on the physical meaning of activation parameters in condensed state, two other functions can be used for expression of these parameters. Their final formulations are applied in Eqs (31) and (32).

$$\beta = \frac{T_i^{m+1}}{A(m+1)} \tag{31}$$

$$\beta = \frac{1}{AD}(e^{DT_i} - 1), \tag{32}$$

where β is heating rate, A, B, D and m are adjustable parameters of temperatures functions and T is temperature. The software Kinpar in the case of Arrhenius temperature function and Origin in the case of non-Arrhenius temperature function was used to calculate the adjustable parameters. These parameters were used in following equations to determine the length of the respective induction periods. Eq. (33) presents Arrhenius temperature function and Eqs (34) and (35) present non-Arrhenius temperature functions.

$$t_i = A\exp(B/T) \tag{33}$$

$$t_i = AT^{-m} \tag{34}$$

$$t_i = Ae^{-DT}. \tag{35}$$

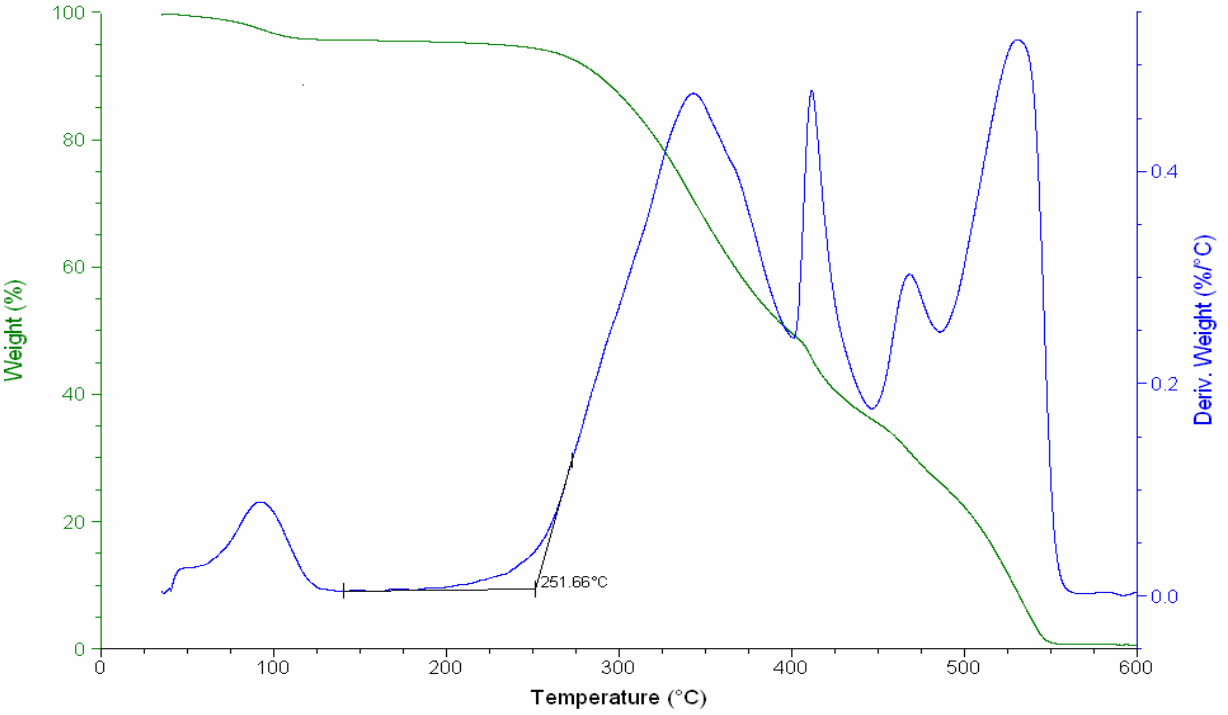

Figure 9 *The thermogravimetric record of thermo-oxidative degradation of sample HA 1 with concentration 5 % in PVA, heating rate 10 K/min, under dynamic oxygen atmosphere 25 ml/min*

5. RESULTS AND DISCUSSION

5.1 Antioxidant efficiency of humic acids of various quality

5.1.1 Antioxidant efficiency of humic acids from several sources

In this part the attempt was paid to learn if the antioxidant effect of humic acids is a general phenomenon for humic acids from various sources, or if the antioxidant properties can be seen only for humic substances extracted from South Moravia lignite used in our previous work [18]. Materials from several deposits differ in composition, content of humic acids and thus in the chemical-physical properties. In this part of the work, we evaluated the antioxidant or pro-oxidant effect of humic acids extracted from various sources.

Thermogravimetry with linear heating was used to evaluate the thermo-oxidative stability of pure PVA and PVA/humic blends. The extrapolated onset degradation temperature seen on DTG was used as a measure of stability of PVA. Mass loss in specific temperature range was considered as a degradability (degradation kinetic) of polymer/humic material. These values and values of onset temperatures are listed in Table 7. Comparison of onset temperatures of PVA and PVA/humic material are given in Figure 10.

Table 7 *Values of onset temperatures of pure PVA and PVA with humic acids from different sources at several concentrations, and mass loss Δm_1 of polymer/humic material from start temperature (40 °C) to onset temperature, mass loss Δm_2 from onset temperature to 300 °C, mass loss Δm_3 from 300 to 400 °C and mass loss Δm_4 from 400 to 500 °C*

Sample	**Concentration (%)**	**Onset temperature (°C)**	**Δm_1**	**Δm_2**	**Δm_3**	**Δm_4**
HA 7	2	253.1	5.20	2.95	50.78	33.32
	5	249.7	4.82	3.46	46.30	28.74
	10	231.6	5.39	5.10	43.41	38.69
HA 22	2	259.1	5.31	2.00	49.53	31.64
	5	255.1	5.76	3.08	43.41	35.17
	10	173.4	4.58	14.76	31.41	39.70
HA 41	2	261.9	4.48	2.67	47.51	28.93
	5	250.9	5.33	5.15	38.49	33.23
	10	215.2	5.33	10.06	30.77	43.11
HA 43	2	258.6	5.24	2.16	50.21	35.47
	5	255.5	5.64	2.80	49.34	37.49
	10	214.0	5.52	5.82	41.70	44.37
HA 44	2	247.1	5.51	4.43	42.21	40.28
	5	253.1	5.41	2.58	49.00	36.33
	10	217.5	4.35	17.30	45.35	27.89
Oxyhumolit	2	256.5	5.22	2.32	51.43	32.68
	5	254.5	4.90	2.83	47.97	30.16
	10	246.8	4.98	3.04	46.74	32.43
Yarikkaya	2	268.4	5.76	1.66	50.30	28.21
	5	265.7	5.21	2.50	45.81	30.20
	10	263.9	8.37	2.66	40.82	33.70
Kasikara	2	265.8	5.31	1.72	51.44	30.74
	5	258.6	6.14	2.22	51.71	31.48
	10	258.0	7.95	2.25	47.40	31.59
PVA		209.5	7.34	3.95	50.86	28.01

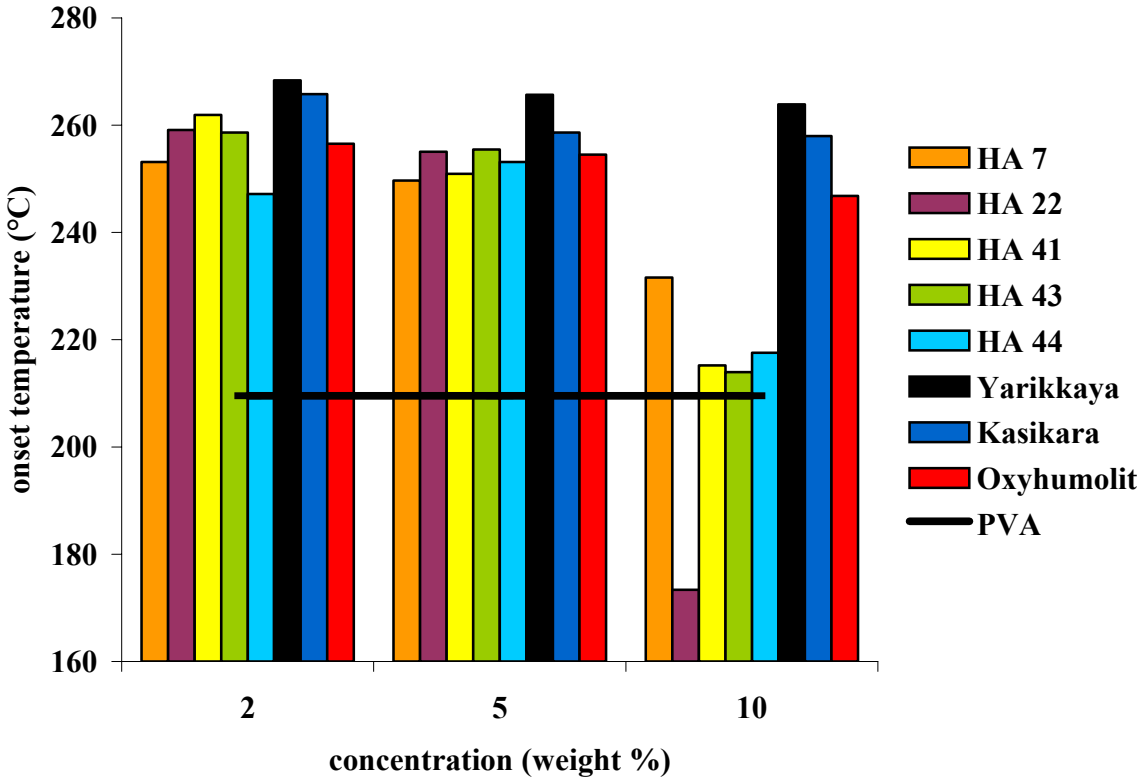

Figure 10 *Onset temperatures as a measure of stability of PVA/humic material from several different sources in comparison with pure PVA (black line)*

Practically in almost all cases, humic acids from different sources showed an increase in stability of PVA except HA 22. In the latter case, the increase in concentration in PVA up to 10 %, the final blend showed a remarkable decrease in stability.

HA 7 represented the peat humic acids. It is noteworthy that the genesis of such humic material is partly similar to that of South Moravian lignite humic acid, and it showed a similar trend in stabilization of humic acid [18]. Further, at concentration 10 % such material showed stronger stabilization efficiency for PVA in contrast to the samples HA 22–44 that can be again explained on the base of the humic material genesis. It is known, that so-called oxyhumolites underwent in the course of their development an intensive oxidation attack, which resulted in the abundance by oxygenated moieties, especially COOH groups. Moreover, such oxyhumolite humic acid is also enriched in aliphatic molecules. Therefore, those are in comparison with lignite and peat humic acids less rich in (poly)phenols content, which are believed to stabilize PVA structure. On the other hand, they posses significantly larger content of unsaturated lipids, which can play role in stabilization processes as well. Thus, the overall antioxidant effect is influenced by a number of factors.

HA 22, HA 41, HA 43 and HA 44 represented humic acids extracted from the same deposit (Figure 8) and showed similar properties and stabilizing effect. In concentration 2 and 5 %, all these acids showed a significant increase in stability. In contrast, at concentration 10 %, they showed only a slight increase in stability; as mentioned above HA 22 showed even destabilizing effect. The processes of destabilization can be attributed to the relatively large

content of oxygen containing functional groups, especially carboxyl groups. At high temperature, the latter are readily decomposed forming free radical responsible for polymer structure destabilization.

A part of this section was also to investigate the influence of type of extraction agent on HA efficiency to stabilize or destabilize PVA structure. Sample HA 41 and Oxyhumolit were obtained from the same source. They differ only in the extraction method, while HA 41 was extracted in the same way as other samples, i.e. by NaOH, the second one was extracted using the pyrophosphate in the mixture with NaOH. Extraction by pyrophosphate caused an increase in content of phenolic groups in the final product [23]. Thus the addition of Oxyhumolit to PVA caused high stabilizing effect in all concentrations.

Remarkable increase of stability showed two Turkish lignite humic acids. In fact they shifted the thermo-oxidative stability of investigated materials at all concentrations more than 45 °C. The reason of such an increase can be seen, among others, in the parent biomass from which were those lignites formed. In contrast to the moderate climate the biomass turnover in a warmer climate supports the quicker turnover, which causes faster degradation of labile molecules such as celluloses, hemicelluloses and proteins. Thus, preferably lignin and other stable molecules take part in humification followed by coalification and as a result, the lignite humic acids contain large amount of lignin-derived, i.e. phenolic moieties. Further, the age of the parental lignite should be taken into account as well.

5.1.2 Antioxidant efficiency of regenerated humic acids

The main goal of this part was the evaluation of the antioxidant or pro-oxidant potential of regenerated humic acids as additives in PVA. In our previous work [18] the antioxidant effect of South Moravian lignite humic acids and its ammonium salts in mixture with PVA was experimentally proved, while addition of sodium salts exhibited a slight pro-oxidant effect at specific concentrations. However, the work dealt with humic acids extracted from lignite. In this part we tried to find out if the oxidative modification of the parental lignite could cause any significant changes in antioxidant efficiency of extracted humic acids.

Again, the thermogravimetry with linear heating was employed to evaluate the thermo-oxidative stability of PVA mixed with regenerated humic acids. As can be seen in the Figure 8 there are several stages of weight loss, which can be attributed to the moisture evaporation at low temperature, and degradation of the polymer at higher temperatures. The extrapolated onset degradation temperature seen on DTG was used as a measure of stability of PVA.

Stability of PVA mixed with regenerated humic acids was assessed and compared using so-called induction period (IP) measurement. The principle of this approach is given in the Experimental part. Application of Arrhenius equation as the temperature function has been demonstrated to be rather complicated due to i) problems with calculation of temperature integral, ii) problems associated with obtaining of unrealistic values of induction periods and moreover iii) adjustable parameters cannot be considered to have a physical meaning. On the other hand, such approach can still be used to model the kinetics of the process although without a deeper insight into its mechanism [44]. Thus besides Arrhenius equation we used

also two non-Arrhenius equations as temperature functions. Obtained parameters were used to calculate the IP using respective equations (Eqs 33–35); detail information is also given in Experimental part. Results were extrapolated to 100 °C (Table 8).

A better estimation of stabilizing effect can be obtained using the ratio of the lengths of induction periods of treated (stabilized) and nontreated material [4], so-called protection factor (PF). Basically, the greater is the value of PF, the higher is the antioxidant effectiveness of the additive. Values of IP and PF of PVA blends with HA and RHA are summarized in Table 8 (Appendixes I and II).

Table 8 *Values of induction period of PVA and PVA/humic material at temperature 100 °C determined by Arrhenius kinetic (AK), non-Arrhenius kinetic with parameters A, D (NAK 1) and non-Arrhenius kinetic with parameters A, m (NAK 2), and values of protection factor (PF) as efficiency of HA and RHA as antioxidants in PVA*

		AK		**NAK 1**		**NAK 2**	
Sample	**Concentration (%)**	**IPx10^3 (year)**	**PF**	**IPx10^3 (year)**	**PF**	**IPx10^3 (year)**	**PF**
HA 1	0.5	5.4	5.8	3.7	30.7	5.4	5.4
	2	11.6	1.7	8.0	83.4	14.5	11.6
	5	2.2	4.6	2.9	13.4	2.3	2.2
RHA 2	0.5	3.5	9.5	6.0	28.1	4.9	3.5
	2	12.0	13.5	8.6	85.0	14.8	12.0
	5	0.7	1.6	1.0	7.0	1.2	0.7
RHA 3	0.5	3.3	4.1	2.6	19.2	3.3	3.3
	2	32.0	49.4	31.3	424.4	74.0	32.0
	5	3.1	0.9	0.6	4.2	0.7	3.1
RHA 4	0.5	2.4	4.5	2.9	14.8	2.6	2.4
	2	9.1	18.2	11.5	94.7	16.5	9.1
	5	0.4	0.9	0.6	3.3	0.6	0.4
PVA		1.0	1.6	1.0	5.7	1.0	1.0

In reference [18] it was demonstrated that addition of humic acids into PVA caused highest increase in stability for concentrations of humic acids 0.5 % and 2 %. On the other hand, when a critical amount of reactive sites is reached (content of free radicals naturally generated by heating), humic acids become to play a role as a pro-oxidant.

From results reported in Table 8, it seems, that the highest efficiency to increase the stability of RHA showed regenerated HA 3 while the most efficient concentration for all regenerated samples was 2 %. Further, results obtained using Eqs (33–35) showed, that all regenerated humic acids in concentration 2 % have higher stabilizing effect than nontreated humic acids. Stabilizing effect increases in sequence HA 1, RHA 2, RHA 4 and RHA 3. Concentration 0.5 % of humic acids also stabilizes PVA. In contrast, 5% addition of regenerated humic acids did not bring a significant change in thermo-oxidative stability. Data obtained from non-Arrhenius temperature function with parameters *A*, *D* shows that nontreated HA 1 causes

slight stabilizing effect, but RHA 3 and RHA 4 show pro-oxidant effect. One can see that data obtained from Arrhenius and non-Arrhenius temperature functions are rather different. Results obtained from non-Arrhenius temperature functions with parameters *A*, *D* can be supposed as more realistic, because they show smaller IP.

In the recent work it can be identified, that in case of South Moravian lignite, the application of 10% nitric acid brought about the largest yield of regenerated humic acids [18]. It means that the latter contains a large number of polar groups responsible for their solubility and which consequently increased the yield of extractable humic matter. Such polar groups are reported mainly phenolic OH groups [46], which is a logical explanation of enhanced efficiency of sample RHA 3.

5.2 Ageing effect on polymer materials

The main goal of this part of the work was to assess whether some significant changes of physical properties take place in pure PVA and PVA mixed with HA and its salts in the course a time period. Humic material is a relatively highly reactive system thus occurrence of interactions between polymer and humic acids is possible. As a result, these reactions can have significant impact on the thermo-oxidation stability of PVA/humic material, both positive and negative. As the most probable we consider the interaction of semichinoidal free radicals, which are uncovered and particularly available to react in sodium humates [18].

As before, thermogravimetry with linear heating was employed. As a measure of possible changes, the extrapolated onset degradation temperature seen on DTG was used. Mass loss was considered as a degradability (degradation kinetic) of polymer/humic material. Obtained values of mass losses and values of onset temperatures are reported in Tables 9–12.

Table 9 *Values of onset temperatures of pure PVA in definite time and mass loss Δm_1 of polymer/humic material from start temperature (40 °C) to onset temperature, mass loss Δm_2 from onset temperature to 300 °C, mass loss Δm_3 from 300 to 400 °C and mass loss Δm_4 from 400 to 500 °C*

Time (week)	Onset temperature (°C)	Δm_1	Δm_2	Δm_3	Δm_4
1	209.6	7.33	3.95	50.86	28.01
2	209.5	4.30	5.07	51.17	30.40
3	208.0	3.58	3.75	55.02	28.64
4	209.1	3.49	5.25	52.59	30.59
5	209.3	3.17	4.65	53.71	28.46
6	208.0	2.72	5.07	54.25	28.60
7	207.7	2.88	5.03	54.28	29.63
9	208.4	3.41	4.54	52.77	30.24
14	208.6	3.16	4.14	53.35	30.02
19	209.4	3.14	4.37	52.93	31.02
24	209.1	2.77	6.21	51.24	27.53
25	209.2	2.80	5.37	50.59	29.91

Table 10 *Values of onset temperatures of PVA/HA blend in definite time and mass loss temperature intervals*

Time (week)	Onset temperature (°C)	Δm_1	Δm_2	Δm_3	Δm_4
1	257.7	9.04	1.60	51.14	32.13
2	257.7	4.25	2.00	53.27	33.63
3	257.6	3.97	1.69	55.08	32.43
4	257.5	3.87	1.99	55.23	33.08
5	257.7	3.45	1.75	55.95	32.45
6	257.8	3.21	2.01	55.03	32.63
7	257.9	3.07	2.37	53.18	34.51
9	257.8	3.79	2.44	50.69	35.84
14	257.7	3.55	1.85	53.18	34.59
19	257.8	3.43	1.97	53.71	33.25
24	257.1	3.08	2.21	53.77	34.29
25	257.2	3.10	2.54	52.23	34.44

Table 11 *Values of onset temperatures of PVA/NaHA blend in definite time and mass loss temperature intervals*

Time (week)	Onset temperature (°C)	Δm_1	Δm_2	Δm_3	Δm_4
1	216.9	7.62	15.53	44.33	28.27
2	216.8	4.21	16.43	46.14	27.99
3	216.6	3.80	17.57	46.13	29.33
4	216.6	3.71	17.06	46.39	30.74
5	217.2	3.71	18.87	43.29	30.82
6	216.8	3.25	17.18	46.97	26.65
7	216.8	2.97	16.02	47.99	28.04
9	216.5	3.68	17.98	46.51	29.17
14	217.2	3.49	19.50	43.10	29.94
19	216.3	3.42	16.59	46.16	28.65
24	216.4	3.93	18.82	45.65	28.18
25	216.9	3.00	18.37	46.68	29.67

Table 12 *Values of onset temperatures of PVA/NH_4HA blend in definite time and mass loss temperature intervals*

Time (week)	Onset temperature (°C)	Δm_1	Δm_2	Δm_3	Δm_4
1	254.5	7.70	3.04	51.78	35.13
2	254.5	4.72	3.47	52.21	37.32
3	254.0	4.31	3.16	52.77	37.56
4	254.2	4.24	3.27	55.77	34.51
5	254.4	3.81	3.52	52.41	35.82
6	253.9	3.50	3.66	53.01	36.78
7	254.7	3.13	4.28	50.00	35.97
9	254.8	3.89	3.30	53.06	35.77
14	254.5	3.72	3.45	52.33	37.10
19	254.5	3.62	3.29	52.43	36.62
24	254.5	3.39	3.19	55.48	36.47
25	254.4	3.23	3.05	55.65	36.53

It is evident, that no reactions, which could influence the thermo-oxidative stability of PVA, were present. It is possible that it was caused by the intensive desiccation, which decreased the moisture and therefore the mobility (diffusion) of HA segments to PVA chains. Larger content of water was observed only in the first measured sample. Later, amount of water decreased and reactions (diffusion) in solid sample diminished. Small variations of onset temperatures and weight loss in specific temperature ranges are within the experimental error.

5.3 TG study of the γ-irradiation on PVA stability after addition of sodium and ammonium salts of humic acids

The main goal of this part was the evaluation of the effect of γ-irradiation on PVA/humic blends thermo-oxidative stability. Degradation of pure polyvinyl alcohol without addition of humates showed a dramatic decrease of stability after γ-irradiation pre-treatment (record not reported).

Examples of thermogravimetric records of thermo-oxidative degradation of irradiated PVA + 2% NH_4HA or NaHA for several days of radiation are given in Figures 11 and 12 (for the rest see Appendixes III and IV).

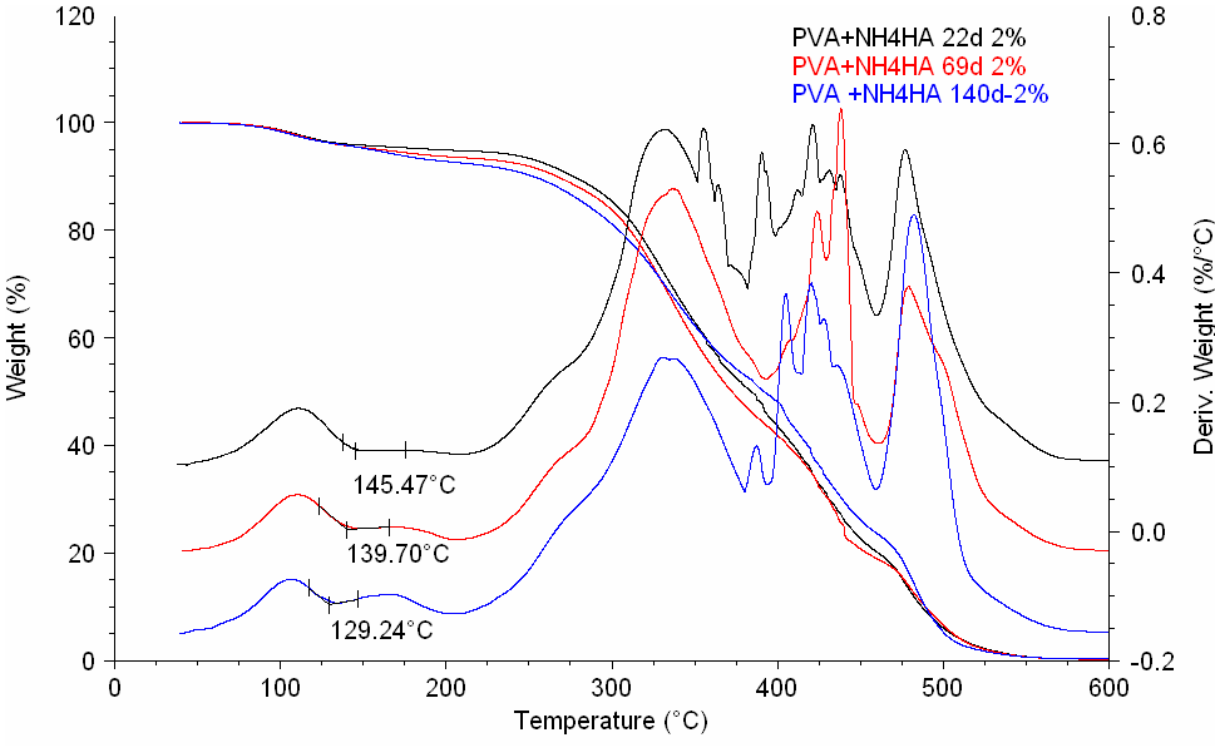

Figure 11 *Comparison of thermogravimetric records of PVA + 2% NH_4HA irradiated 22, 69 and 140 days, with respective dosages 127, 430 and 806 kGy*

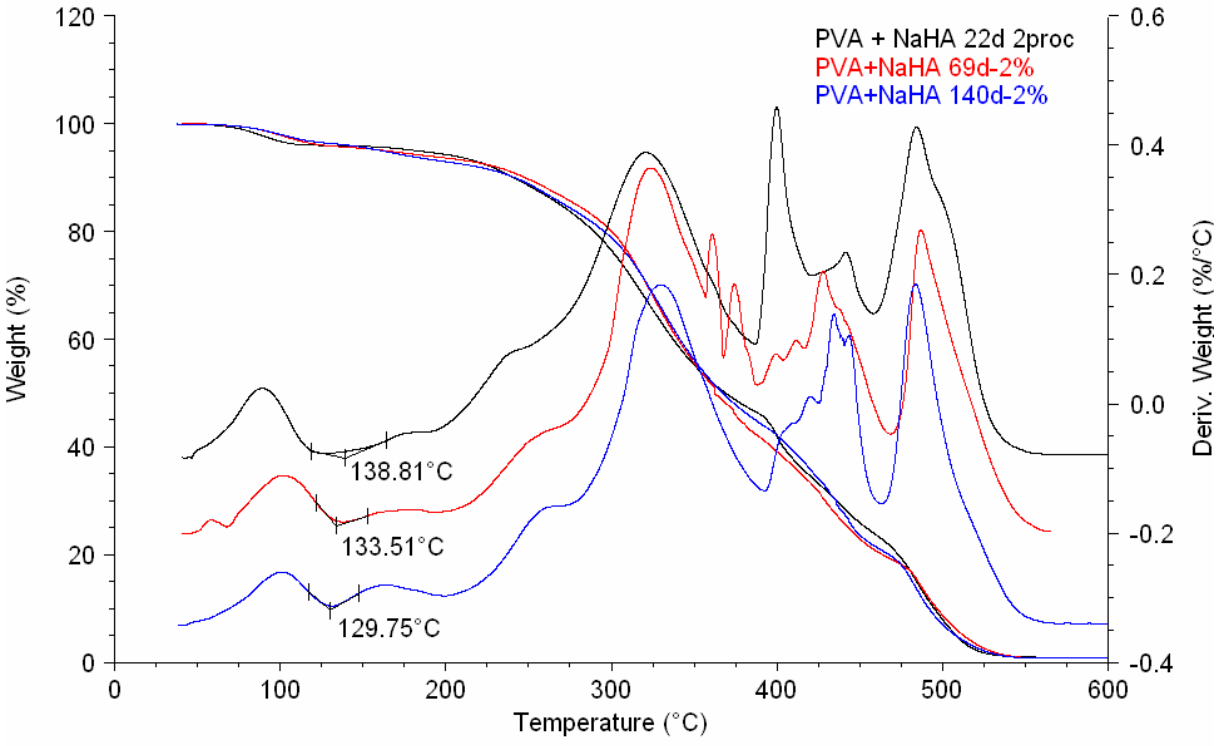

Figure 12 *Comparison of thermogravimetric records of PVA + 2% NaHA irradiated 22, 69 and 140 days, with respective dosages 127, 430 and 806 kGy*

As we reported earlier the non-irradiated PVA blend enriched by 2% ammonium humate is stable up to 218 °C [18], therefore, the gamma irradiation causes the decrease in stability of PVA already after 22 days of exposition. Similarly, in the case of non-irradiated PVA with addition of 2% NaHA, which stabilizes PVA up to 196 °C, γ-irradiation causes destabilization of polymer/NaHA blend. It is noteworthy, that low-concentrated ammonium humate enriched samples showed relatively high stability even after 140 days of irradiation. Although a small decreasing tendency is evident, it seems that ammonium humate still exhibits an antioxidant effect. In contrast, remarkable decrease in stabilization efficiency can be seen for concentrations above 2 %. Conversely, sodium humates PVA blends showed progressive destabilization after 22 days, which continued within 140 days of the exposition for all concentrations. Such observations and conclusions are in agreement with our result reported in reference [18].

The second parameter, which can be evaluated from a thermogravimetry record, is the degradability (rate of degradation), which is proportional to values of DTG (2nd Y axe in the Fig. 11 and 12). Thus, obtained results indicate that although after the irradiation the degradation started significantly earlier, however, when the degradation already started, the material which was exposed to longer γ-irradiation degrades more slowly than the original one [18].

Table 13 *Values of onset temperatures of PVA + NH_4HA in several concentrations. Comparison of non-radiated and γ-irradiated samples*

Dosage (kGy)	**Concentration of NH_4HA in PVA**					
	0.5 %	**1 %**	**1.5 %**	**2 %**	**5 %**	**10 %**
0	218.7	219.0	218.6	218.7	216.6	214.2
22	132.9	132.5	116.3	145.5	130.4	144.0
36	133.6	133.8	123.5	146.0	119.8	133.0
41	131.3	133.5	105.7	145.6	124.7	137.6
55	133.8	128.0	128.9	137.1	132.5	142.1
69	133.7	132.7	129.9	139.7	125.5	137.5
84	133.9	127.6	127.4	149.4	132.4	130.6
91	126.9	133.7	123.1	117.1	128.4	115.1
105	135.2	123.0	128.5	146.0	129.5	111.6
140	132.7	128.5	126.6	129.2	126.7	118.5

Table 14 *Values of onset temperatures of PVA + NaHA in several concentrations. Comparison of non-radiated and γ-irradiated samples*

Dosage	**Concentration of NaHA in PVA**					
(kGy)	**0.5%**	**1%**	**1.5%**	**2%**	**5%**	**10%**
0	199.9	194.6	195.3	196.5	195.5	192.9
22	137.6	131.6	140.2	138.8	144.8	147.8
36	123.9	126.2	134.8	129.8	130.0	130.5
41	105.4	119.2	121.7	131.2	132.6	148.5
55	135.4	131.0	135.3	136.4	133.7	122.4
69	116.7	108.4	129.0	133.5	131.2	142.4
84	131.4	112.9	130.5	134.7	120.6	147.1
91	129.9	133.7	126.6	119.8	124.4	144.5
105	128.7	110.5	131.0	115.7	128.8	129.1
140	126.0	106.1	111.3	129.8	109.7	126.0

It is noteworthy, that pure lignite humic acids in all forms are rather resistant to γ-irradiation at relatively high exposure dose [48]. That is in contrast to their effect in PVA blends. We hypothesize that despite the similarity in thermo-oxidative degradation profiles (Figures 11 and 12), mechanisms of antioxidative protection is different and thus resulted in different antioxidant efficiency of respective humates.

According to literature data, this shift in temperature to lower values means a decrease in durability of a material. In other words, in case of application of sodium and ammonium salts as additives into polyvinyl alcohol matrix, the γ-irradiation can be used to prepare a material with predictable properties and significantly lower stability. Lower stability together with the high degradability can play a significant role in the selection of a proper material especially in case of environmental applications where the further material stability after expiration date is undesirable.

6. CONCLUSION

It has been demonstrated that antioxidant properties are a general phenomenon for humic acid from various sources. Thermo-oxidative stability of polymer/humic material was evaluated by means of thermogravimetry. All measured samples with concentration 2 and 5 % of humic acids showed a positive effect on the stability of PVA. At higher concentrations, humic acids showed a slight pro-oxidant effect causing destabilization of the investigated polymer.

Thermal stability expressed as the length of induction period of PVA with addition of humic acids was assessed by means of thermogravimetry and using a mathematical apparatus of isoconversional method. For the calculation of the induction period, 3 temperature functions were used, while non-Arrhenius temperature function NAK 1 showed the most realistic results. It is evident that exponential dependence in Arrhenius temperature function can lead to non-realistic result after extrapolation to lower temperatures. Stabilities of PVA enriched with 3 regenerated humic acids were compared with PVA blend mixed with humic acids extracted from non-pretreated lignite. Obtained results showed, that all regenerated humic acids in concentration 2 % had greater stabilizing effect than humic acid extracted form paternal lignite. Stabilizing effect increased in sequence HA 1, RHA 2, RHA 4 and RHA 3. Concentration 0.5 % of humic acids also stabilized PVA. In contrast, 5% addition of regenerated humic acids did not bring significant increase of stability.

Ageing effect on PVA/humic blend showed no changes in thermal properties, which indicated no additional reactions between humic acids and PVA.

Further, it has been demonstrated the potential of lignite humic acids and its salts as the potential antioxidants for γ-irradiated PVA. Obtained results indicated that humic acids were not significantly influenced by the long-term exposition of γ-irradiation in comparison with pure PVA and they still could, or at least partly, stabilize the polymer material. Changes in stability are promising with regards to development of materials used in environment and agriculture with predictable lifetime durability and degradability.

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8. LIST OF ABBREVIATIONS

ACC	alternating current calorimetry
AK	Arrhenius kinetic
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTG	derivative thermogravimetric (analysis)
ESI	electrospray ionisation
ESR	electron spin resonance
FA	fulvic acid
FTIR	Fourier infrared (spectroscopy)
FWO	Flynn-Wall-Ozawa
GPC	gel permeation chromatography
HA	humic acid
HPSEC	high-performance size-exclusion chromatography
HS	humic substances
ICTAC	International Confederation for Thermal Analysis and Calorimetry
IHSS	International Humic Substances Society
IP	induction period
KAS	Kissinger-Akahira-Sunose
MS	mass spectroscopy
NAK 1	non-Arhenius kinetic with parameters A, D
NAK 2	non-Arhenius kinetic with parameters A, m
NMR	nuclear magnetic resonance
OIT	oxidation induction time
OOT	oxidation onset temperature
PVA	polyvinyl alcohol
PF	protection factor
RHA	regenerated humic acid
SOM	soil organic matter
TA	thermal analysis
TG	thermogravimetry
TMA	thermomechanical analysis
TMAH	tetramethylammonium hydroxide
TL	thermoluminescence
TSC	thermostimulated current
UV	ultraviolet (spectroscopy)

9. LIST OF APPENDIXES

9.1 Appendix I

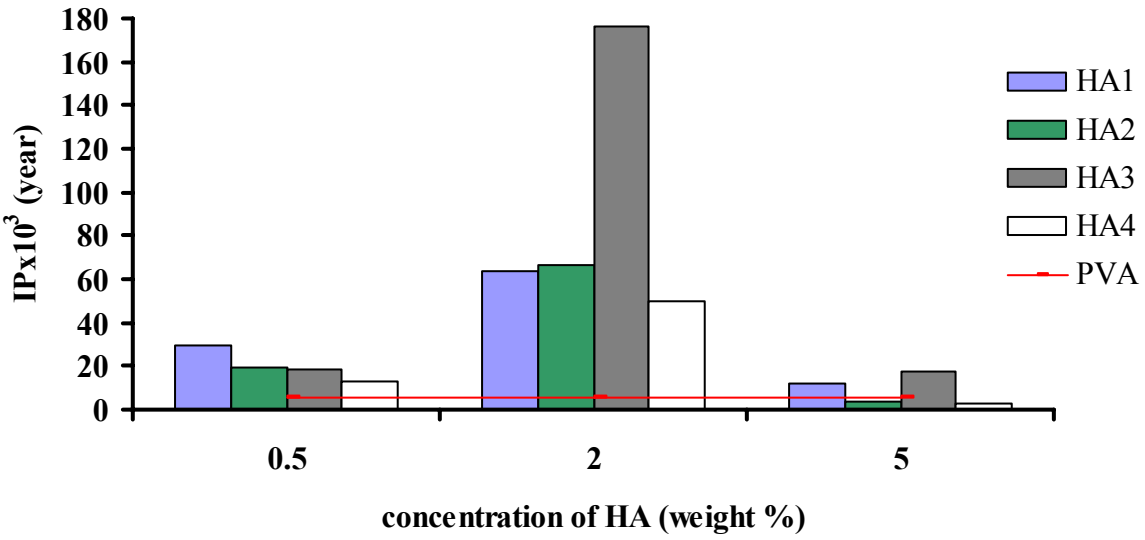

Figure 9.1.1 *Induction period determined by AK at 100 °C*

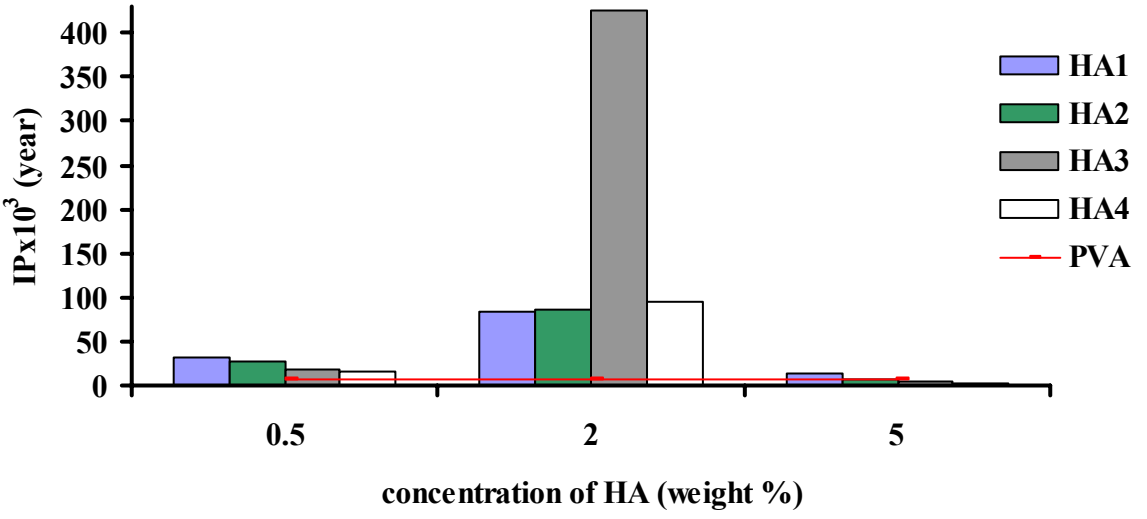

Figure 9.1.2 *Induction period determined by NAK 1 at 100 °C*

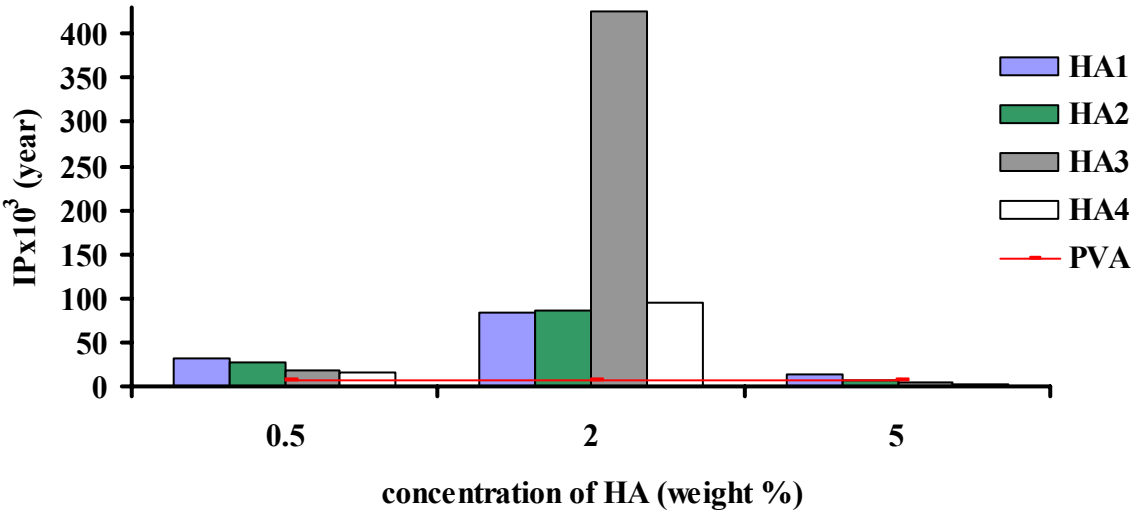

Figure 9.1.3 *Induction period determined by NAK 2 at 100 °C*

9.2 Appendix II

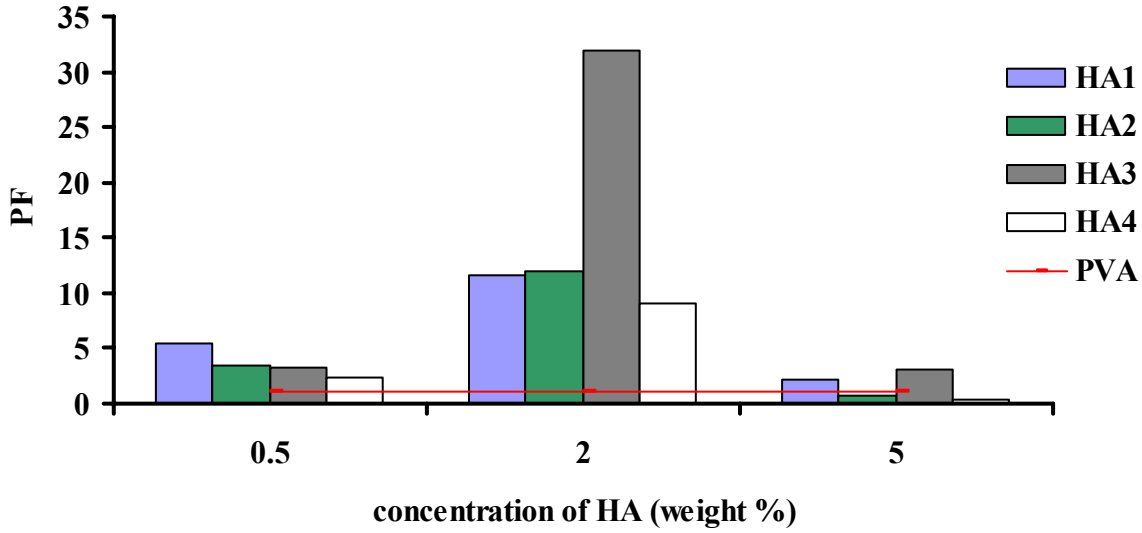

Figure 9.2.1 *Protection factor determined by AK*

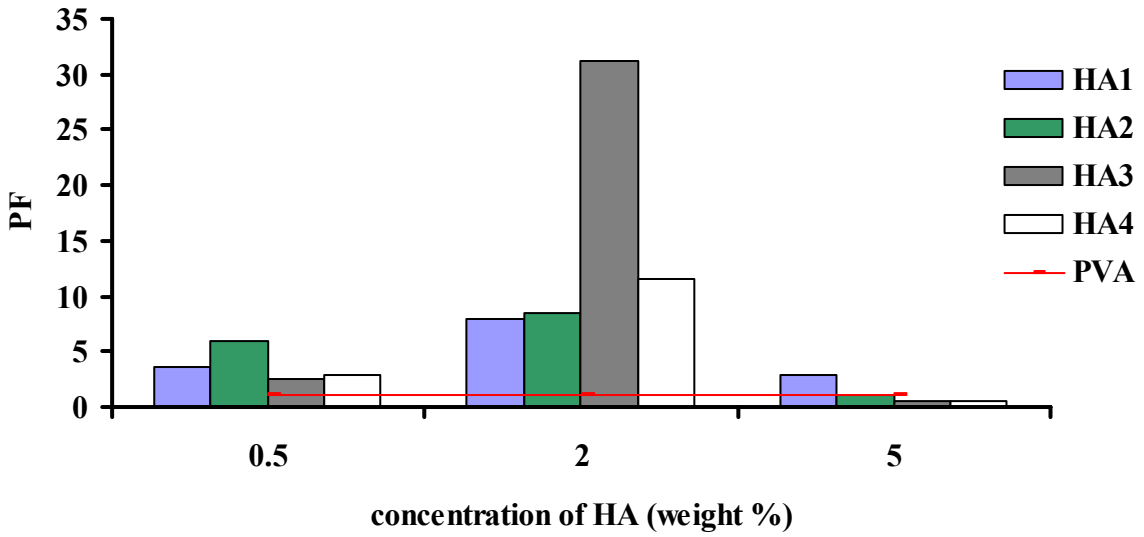

Figure 9.2.2 *Protection factor determined by NAK 1*

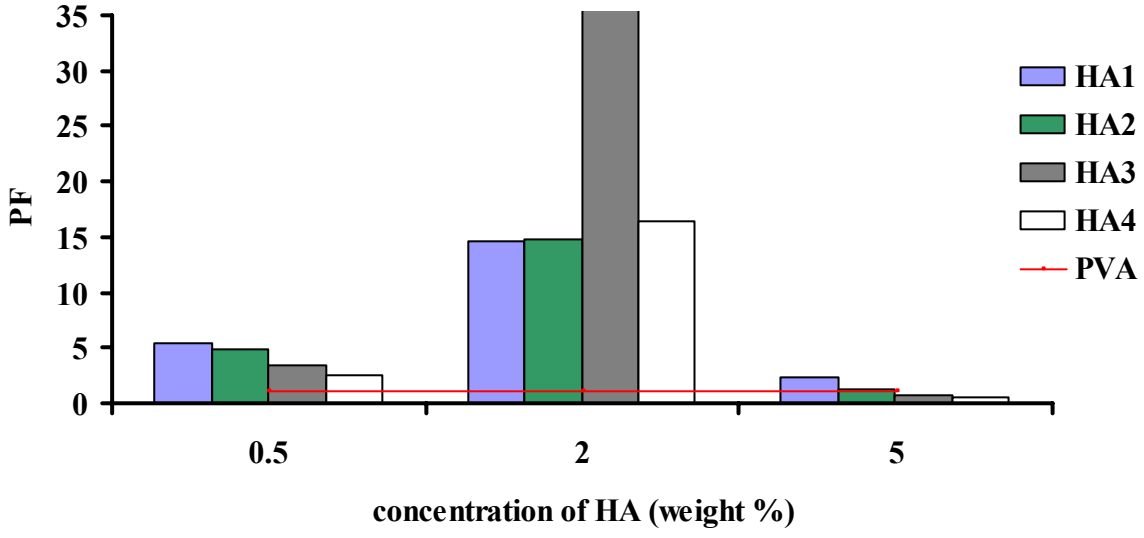

Figure 9.2.3 *Protection factor determined by NAK 2*

9.3 Appendix III

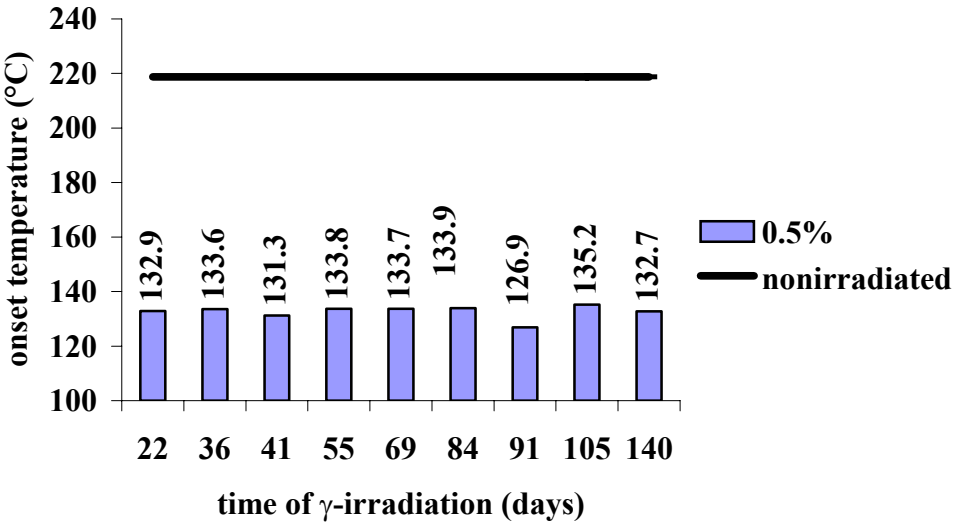

Figure 9.3.1 *γ-irradiation of PVA with 0.5% NH_4HA*

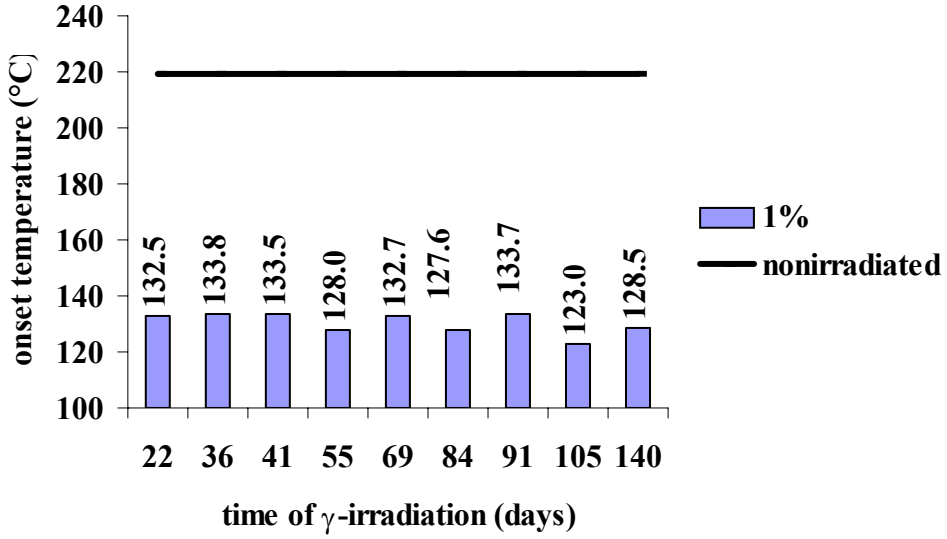

Figure 9.3.2 γ-irradiation of PVA with 1% NH_4HA

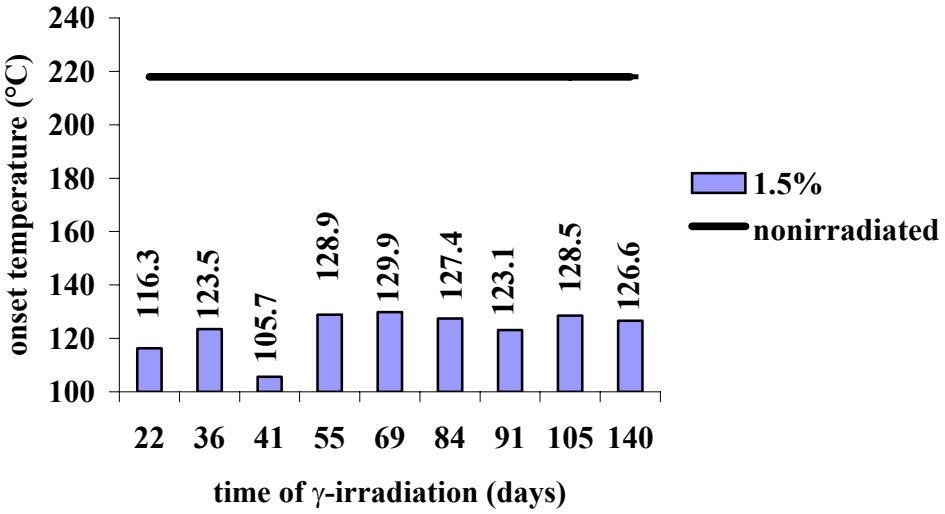

Figure 9.3.3 *γ-irradiation of PVA with 1.5% NH_4HA*

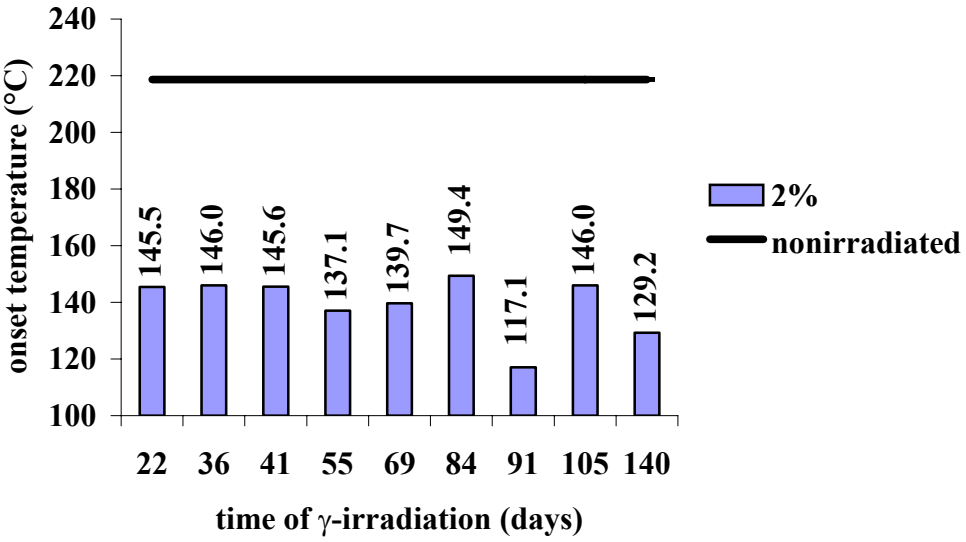

Figure 9.3.4 *γ-irradiation of PVA with 2% NH_4HA*

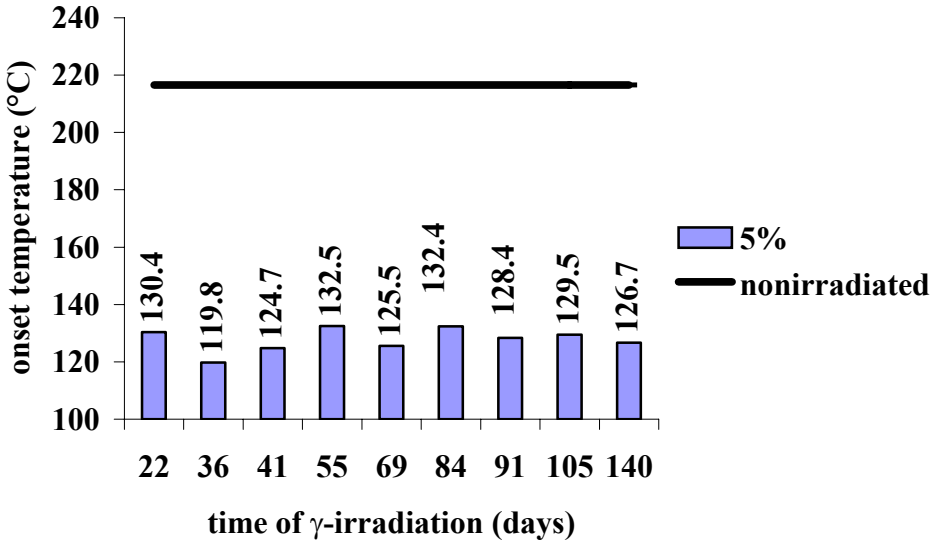

Figure 9.3.5 *γ-irradiation of PVA with 5% NH_4HA*

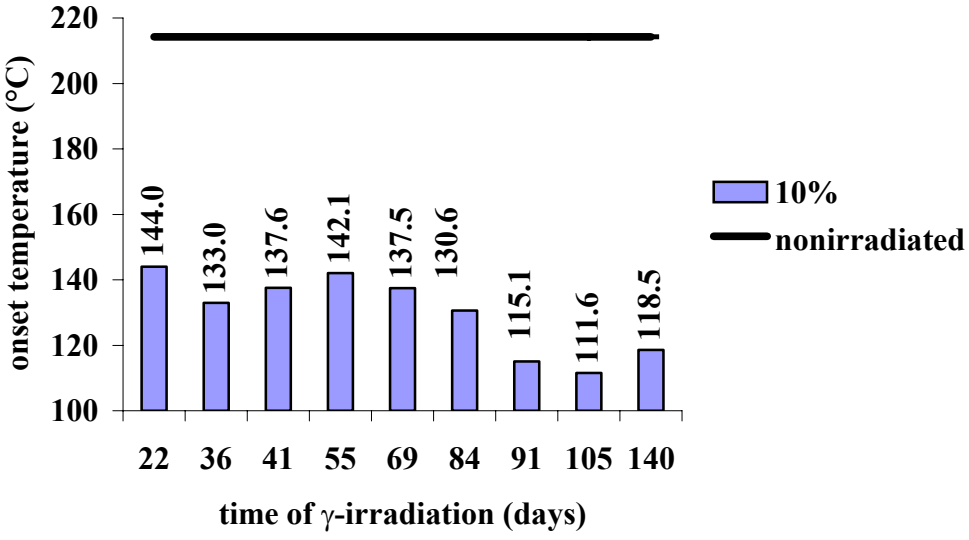

Figure 9.3.6 *γ-irradiation of PVA with 10% NH_4HA*

9.4 Appendix IV

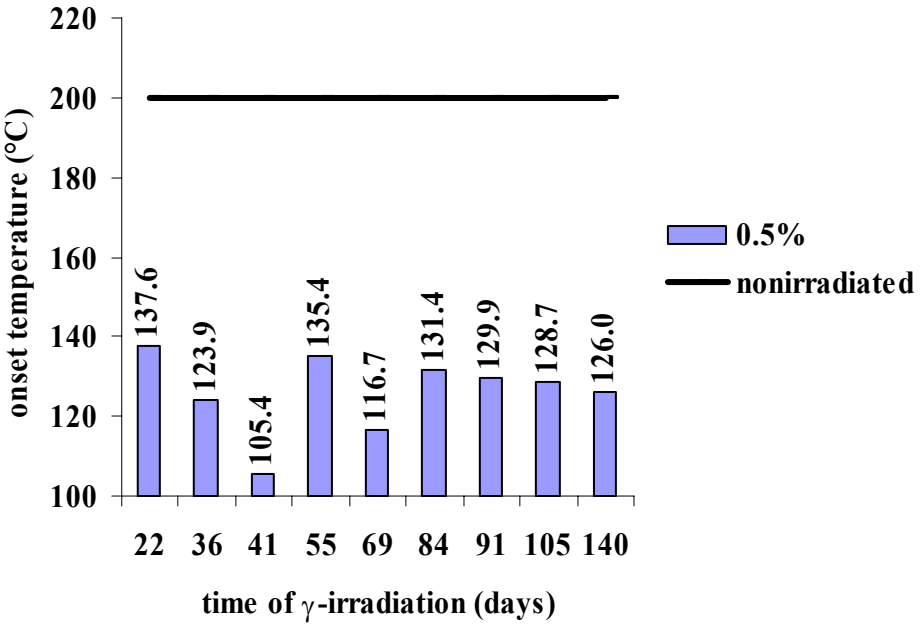

Figure 9.4.1 *γ-irradiation of PVA with 0.5% NaHA*

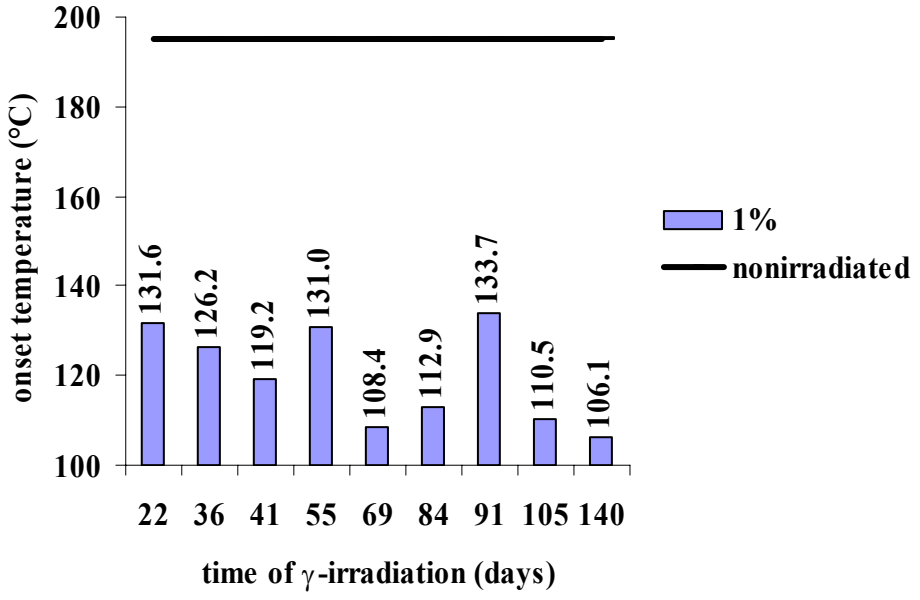

Figure 9.4.2 *γ-irradiation of PVA with 1% NaHA*

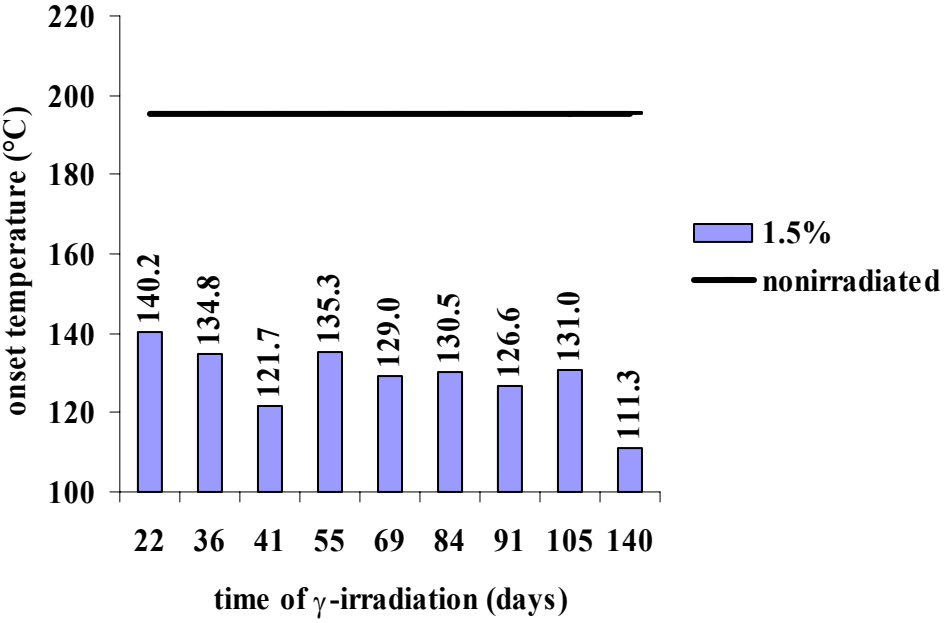

Figure 9.4.3 *γ-irradiation of PVA with 1.5% NaHA*

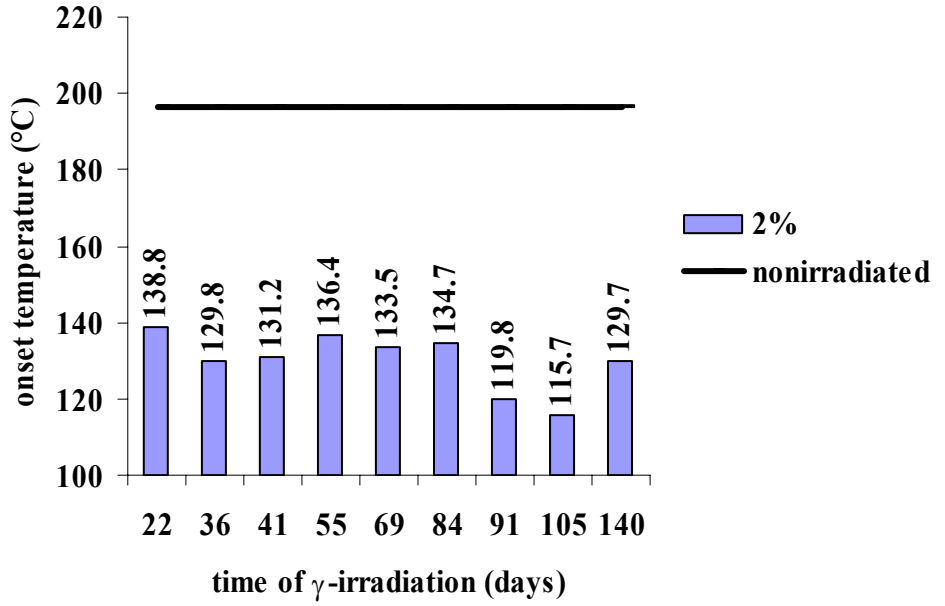

Figure 9.4.4 *γ-irradiation of PVA with 2% NaHA*

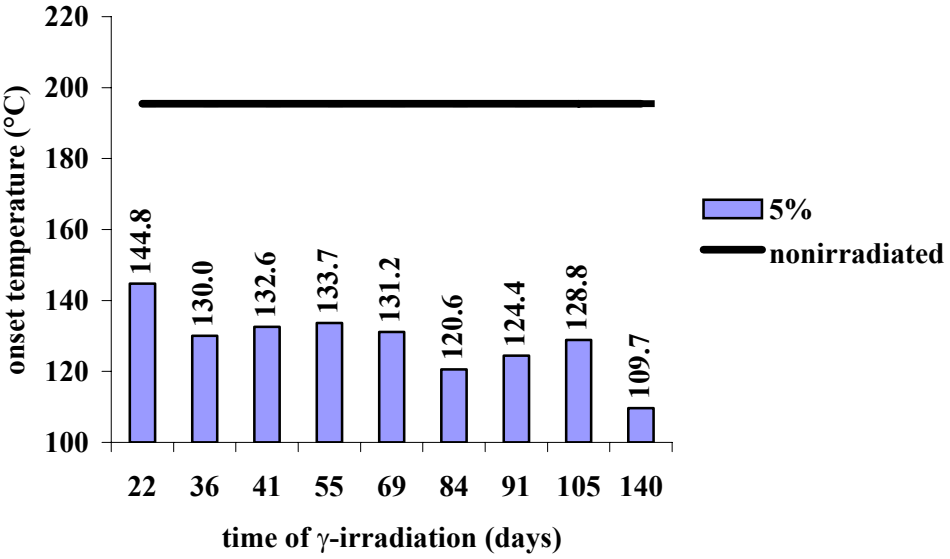

Figure 9.4.5 *γ-irradiation of PVA with 5% NaHA*

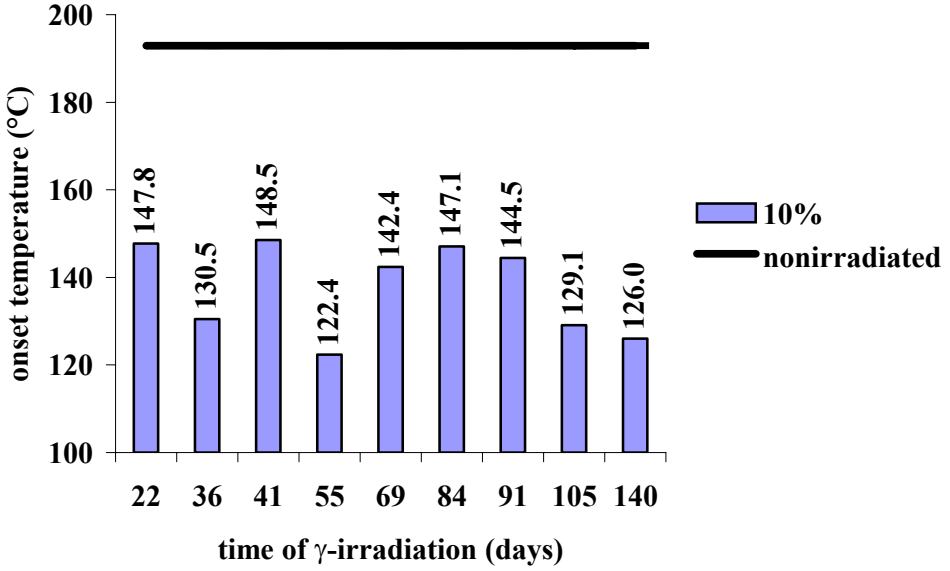

Figure 9.4.6 *γ-irradiation of PVA with 10% NaHA*

9.5 Appendix V

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